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NEW BAND SYSTEM OF TITANIUM OXIDE[1]

By ANDREW CHRISTY

ABSTRACT

Fowler has shown that the characteristic bands of the M-type stars are due to an oxide of titanium. They are usually referred to in the literature as TiO_2 bands. They extend in stellar spectra from λ 4352 to λ 7500. It has been shown by the writer that the bands occurring in the blue-and-green region of the spectrum are due to neutral TiO, and in particular to a $^3P - ^3P$ electronic transition.

In addition to the foregoing region, there were numerous unassigned bands in the yellow and red. These have now been arranged in a new system, whose lower level is the same as that of the blue-green system. There is evidence that Q-branches are present in these bands, indicating that the transition is probably a $^3P - ^3S$.

The frequency of vibration for infinitesimal amplitude is found to be 862.5 and 1003.8 cm^{-1}, for the upper (initial), ^3S, and lower (final), ^3P, states, respectively. The moment of inertia of the molecule in the ^3S-state is estimated to be about 54.8×10^{-40} g.cm^2. The corresponding nuclear separation is 1.66×10^{-8} cm. The heat of dissociation for the lowest level, with linear extrapolation, is 6.74 volts.

These two systems are both resonance systems of the TiO molecule. It is known that the titanium bands persist in stellar spectra up to 3300 T°. At this temperature the product of the partial pressure of titanium and oxygen divided by the partial pressure of titanium monoxide is 10^{-3} atmospheres. Assuming that with the instruments used in stellar spectroscopy, the titanium bands will not be observable if the ratio of Ti to TiO is as 100 to 1, we find that the partial pressure of oxygen in stellar reversing layers is about 10^{-6} atmospheres.

INTRODUCTION

In 1904 A. Fowler[2] obtained the band spectrum of an oxide of titanium extending from about λ 4350 to λ 7200, and was able to show that all the prominent bands appearing in M-type stars were due to the foregoing molecule. Up to that time the known bands in

[1] Preliminary account of this work has been given in a letter to *Nature* dated April 22 (in press).

[2] *Proceedings of the Royal Society*, A, **73**, 219, 1904; A, **79**, 509, 1907.

this particular type of stellar spectra extended from λ 4352 to λ 5860.

C. Shane[1] rephotographed the spectrum of *o* Ceti, extending the region to λ 6679, and identified a large number of bands with the known bands of titanium oxide. Bands due to this molecule, especially in the yellow-and-red portion of the spectrum, have been observed in the sun-spots by Hale and Adams.[2] P. W. Merrill[3] found that the most characteristic bands of the M-type stars, in the red portion of the spectrum, are in the region λ 7050 to λ 7200. He also discovered a band at λ 7500, and, by obtaining the spectrum of titanium oxide in the arc in the foregoing region, was able to show that the latter belonged to the same molecule.

It has been shown that the bands occurring in the blue-and-green part of the spectrum are due[4] to neutral TiO, and, in particular, to a $^3P - {}^3P$ electronic transition. Quantum numbers have been assigned to both the vibrational and rotational levels of the two states involved. The mean separation of the triplets was found indirectly to be about 70 cm^{-1}.

After the completion of the work in the blue-green region, an investigation of the remaining bands was undertaken, in order to ascertain the quantum assignment of these bands. Dr. Merrill kindly put at the writer's disposal prints of the new bands of titanium oxide which he had photographed.

MEASUREMENTS OF PLATES

The heads of these bands were measured on a 200-mm Gaertner comparator.[5] For the region of λ 7500, since no plate was available, the measurements were made with a glass negative made from a print. The print itself was made from a spectrogram of the titanium arc, taken in the second order of a ten-foot concave grating by Dr.

[1] *Lick Observatory Bulletin*, No. 335, 1919.

[2] *Astrophysical Journal*, 25, 75, 1907.

[3] *Bureau of Standards Science Papers*, 14, 487, 1919.

[4] Birge and Christy, *Physical Review*, 29, 212, 1927; A. Christy, *ibid.*, 33, 701, 1929.

[5] This comparator was purchased with a grant made to R. T. Birge from the Rumford Committee of the American Academy of Arts and Sciences.

PLATE I

The New System of *TiO*
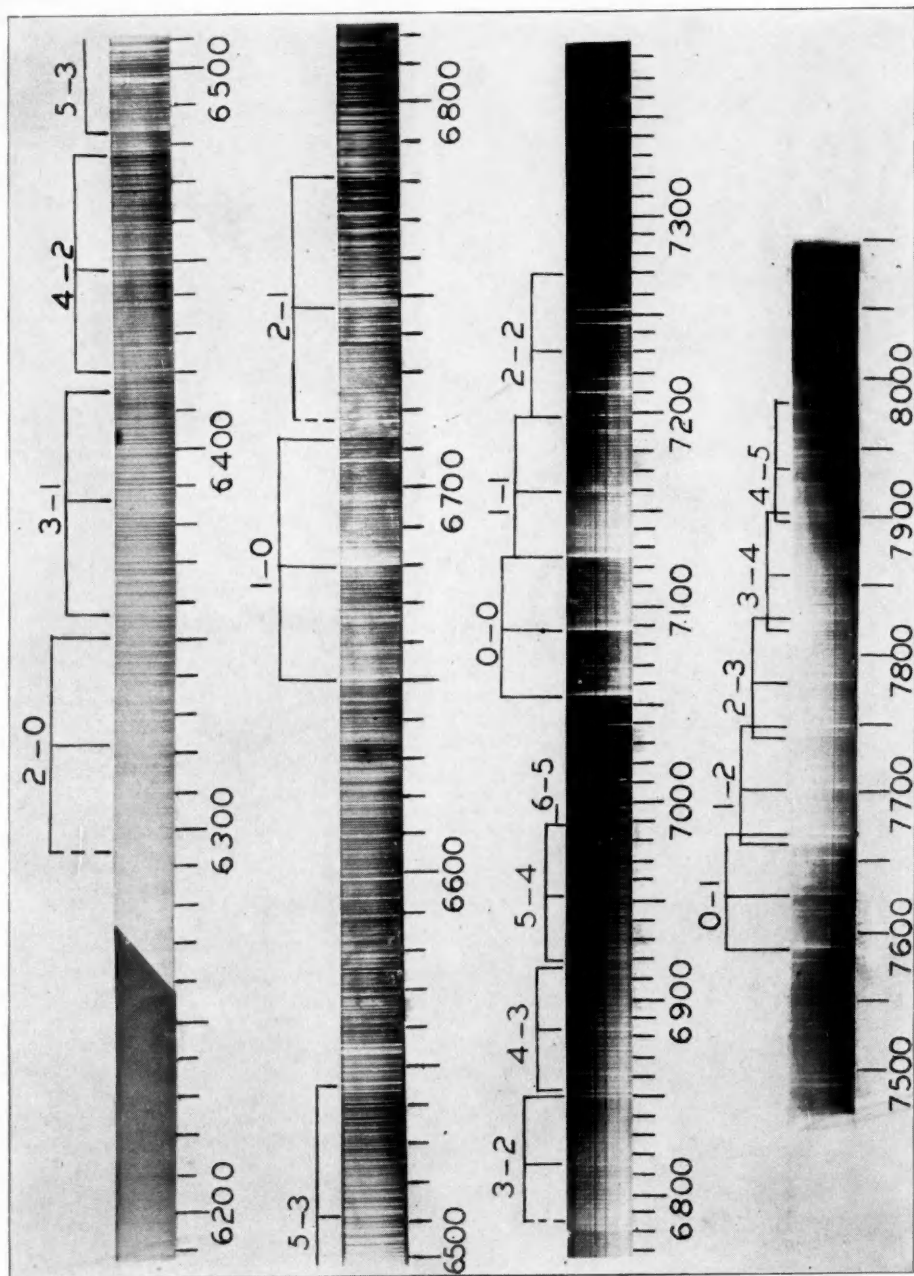
Merrill at the Bureau of Standards. A few heads at λ 7200 to λ 7300 were obtained from a similar negative. The remaining heads have been measured from an arc plate sent to the writer by Dr. A. S. King. As standards, titanium lines were used. The values are those given by K. Behner,[1] and Kiess and Meggers.[2] Most of the heads are very weak. On the whole, the accuracy of the measurements is not expected to be better than 1 cm^{-1}.

VIBRATIONAL ANALYSIS

It has been remarked that the characteristic bands of the M-type stars, in the red portion of the spectrum, are those occurring at about λ 7050. This group of bands, which at first was thought to belong to a regular sequence, shows a peculiar intensity distribution, as can be seen clearly in Plate I. The intensity of the third band in the series is slightly greater than those of the first two, whose intensities are about equal. The fourth band is considerably weaker. The next sequence, occurring at about λ 7500, again shows certain anomalies. The third band seems to have two almost equally strong heads. The first, second, and fourth have single heads, while the fifth has apparently two heads. It was noted that the intervals between the first three more intense bands of the two sequences were about 70 cm^{-1}. From the analysis of the blue-green system, it was known that intervals of this magnitude would occur, if we were dealing with transitions from either of the known states to a new single state. With these considerations in mind, it was comparatively easy to arrange the bands into a system. It was shown that the first three heads were due to three components of the same band. In the λ 7050 group, the third head of the first band almost coincides with the first head of the following band in the sequence. In Merrill's plate these two heads cannot be separated, although Fiebig[3] gives measurements of two separate heads in this region.

The new titanium system consists of 22 bands, containing 52 heads, extending from λ 5737 to λ 7988, and partially overlapping

[1] *Zeitschrift für wissenschaftliche Photographie*, **23**, 326, 1925.

[2] *Bureau of Standards Science Papers*, **16**, 51, 1920.

[3] P. Fiebig, *Zeitschrift für wissenschaftliche Photographie*, 8, 73, 1910.

the bands of the blue-green region. The equation based on the heads measured by the writer is[1]

$$\nu = \begin{Bmatrix} 14172.2 \\ 14105.8 \\ 14030.8 \end{Bmatrix} + (862.5n' - 3.84n'^2) - (1003.8n'' - 4.61n''^2), \quad (1)$$

the average observed *minus* calculated value being 1 cm^{-1}. The equation for the blue-green system was published[2] as

$$\nu = \begin{Bmatrix} 19349.34 \\ 19347.44 \\ 19338.61 \end{Bmatrix} + (833.31n' - 4.546n'^2) - (1003.60n'' - 4.519n''^2). \quad (2)$$

Thus it is seen that the lower level is common to both systems.

The quantum designation, wave-length, frequency, and the observed *minus* calculated values based on equation (1) are given in Table I, columns 1, 2, 3, and 4. Following a procedure used previously, the heads are designated by a, b, and c. The designation is purely empirical. Most of these heads are given by both Fowler and Fiebig, and have been remeasured by the writer. Many of these have been found by Shane[3] in the spectrum of o Ceti. At least four heads belonging to three bands unidentified by Shane are shown to belong to the new system. Definite intensity values cannot be assigned to the bands of this system, as separate portions were taken under different conditions. One may say, however, that the intensity distribution is somewhat similar to that found in the blue-green system.

In the latter system, by the use of Hill and Van Vleck's formulae,[4] the mean separation of the lower levels was shown indirectly to be 70 cm^{-1}. The mean separation of the heads obtained from equation (1) is 70.7. The difference is well within the experimental error. Thus it is apparent that the upper level of the new system is single, or, if multiplet, its various components must lie very close to each other.

[1] In obtaining equation (1), the mean values of ω'', gotten from both systems, were used. However, if the values of ω'' derived from the new system alone had been used, the values of the constants would have been the same within the experimental error.

[2] A. Christy, *Physical Review*, **33**, 701, 1929.

[3] *Op. cit.*   [4] *Physical Review*, **32**, 261, 1928.

TABLE I

THE NEW TITANIUM BAND SYSTEM

$n'-n''$	λ_{air} (I.A.)	ν_{vac} (cm^{-1})	O−C (cm^{-1})	$n'-n''$	λ_{air} (I.A.)	ν_{vac} (cm^{-1})	O−C (cm^{-1})
0-1	a 7589.1	13173.6	+0.6	2-0	a 6294.2	15883.2 S	+1.3
	b 7627.7	13106.5	− .1		b 6321.4	15814.8	−0.7
	c 7671.5	13031.6	± .0		c 6350.4	15742.7	+2.2
1-2	a 7666.0	13041.0	− .8	3-1	a 6357.5	15725.1	−0.9
	b 7704.8	12975.3	±0.0		b 6384.4	15658.6	−1.0
	c 7751.6	12897.0	−3.3		c 6415.8	15583.1	−1.5
2-3	a 7742.8	12911.7	−0.3	4-2	a 6419.8	15572.5 S	+0.8
	b 7782.7	12845.5	− .1		b 6447.8	15505.0	+ .3
	c 7828.1	12771.0	+ .5		c 6478.8	15430.6 f	+ .3
3-4	a 7820.3	12783.7	− .1	5-3	a 6483.5	15419.4	+0.5
	b 7860.5	12718.3	+ .9		b 6512.2	15350.8	−1.7
	c 7907.5	12642.7	+0.3		c 6544.1	15276.8	−0.7
4-5	a 7898.0	12657.9	+1.0	6-4	a 6549.0	15265.3 S	−2.3
	b 7938.5	12593.4	+1.7	5-2	c 6148.8	16259.0	+0.8
	c 7987.7	12515.8	+0.3				
0-0	a 7054.3	14171.8	− .4	3-0	b 6000.0	16662.1 S	+3.5
	b 7087.7	14105.1	− .7				
	c 7125.5	14030.2	− .6	4-0	b 5717.5	17485.3 S	−9.1
1-1	a 7124.9	14031.4 f	− .3		c 5736.7	17427.1 S	+7.7
	b 7158.5	13965.6	+ .3				
	c 7197.2	13890.5	+0.2	Calculated Values			
2-2	a 7197.2	13890.5	−2.2	0-2	a 8206	12183.0	
	b 7230.8	13825.9	−0.4		b 8251	12116.2	
	c 7270.4	13750.6	− .7		c 8302	12041.2	
1-0	a 6651.3	15030.5	− .4	1-3	a 8289	12061.0	
	b 6680.8	14964.2	− .3		b 8335	11994.2	
	c 6713.9	14890.4	+0.9		c 8387	11919.2	
2-1	a			0-3	a 8924	11202.3	
	b 6746.7	14818.0	+1.7		b 8978	11135.5	
	c 6781.3	14742.3	+1.0		c 9049	11060.5	
3-2	a			1-4	a 9015	11089.5	
	b 6814.7	14670.1	+0.5		b 9069	11022.7	
	c 6849.9	14594.6	± .0		c 9132	10947.7	
4-3	a 6852.1	14590.1	−0.8				
	b 6883.6	14523.3	−1.2				
	c 6918.9	14449.3	−0.2				
5-4	a 6919.1	14448.8 F	+1.1				
	b 6951.5	14381.4 F	+0.4				
	c 6988.6	14305.1	−0.9				

F = Fowler's measurements (converted to I.A.).
f = Fiebig's measurements (converted to I.A.).
S = Shane's measurements in I.A.

It is questionable whether the unequal separation as given by the heads, i.e., 66.4 and 75.0 cm^{-1}, corresponds to the actual separation of the origins. We would expect theoretically, to a first approximation, the two intervals to be equal if the upper level is single. However, this rule need not hold rigidly in molecules any more than the corresponding interval rule holds rigidly in atoms.

As has been noted, the blue-green bands are probably due to a $^3P - ^3P$ transition. Hence the lower level of the new system is a ^3P. The structure of the new bands, as far as can be ascertained by a cursory examination, seems to be fairly simple. Many of the more intense heads have clearly marked secondary heads, formed presumably by a Q-branch, indicating that the upper level is probably an S-level. Transitions from singlets to triplets occur rarely in band spectra, and when they do they generally give rise to very weak bands. The bands of this system, however, are quite strong. They must be due therefore to a $^3P - ^3S$ transition. The distance between the primary and secondary heads is, on the average, 10 cm^{-1}. Assuming that the R-branch is given with sufficient accuracy for low-quantum numbers by

$$\nu = \nu_0 + 2B'm + Cm^2 , \tag{3}$$

we may obtain the quantum number m of the head by differentiating the foregoing equation and setting the result equal to zero. Thus, we find that $m = -B'/C$. Therefore

$$\nu - \nu_0 = 10 = -2B'^2/C + B'^2/C = -B'^2/C .$$

Since $C = B' - B''$ and $B'' = 0.53377$, we have

$$B'^2 + 10B' - 5.3377 = 0 . \tag{4}$$

From this we obtain $B' = 0.505$, $I_0' = 27.70/0.505 = 54.8 \times 10^{-40}$ g.cm^2, and $r_0' = \sqrt{I/\mu} = 1.66 \times 10^{-8}$ cm, where μ is the reduced mass of the molecule. These values are not expected to be very accurate, but undoubtedly B' is good to within 1 per cent, hence r_0' is good to $\frac{1}{2}$ per cent.

Both these systems are found in absorption in stellar spectra of the M-type stars. Considering the temperatures of stellar atmospheres in which all these bands occur, it is evident that the two

systems are resonance systems of the *TiO* molecule. It is known
that generally the normal state of the molecule gives a linear $\omega_n : n$
curve, therefore the value, 6.74 volts, for the lower level, obtained
by the method of Birge and Sponer,[1] cannot be greatly in error.
A linear extrapolation of the ^3S- and upper ^3P-levels (Fig. 1) gives
6 and 4.8 volts, respectively. The latter two values are very rough
approximations. Adding to the foregoing two values the equivalent·
energy in volts of the o–o band for each system, we obtain about
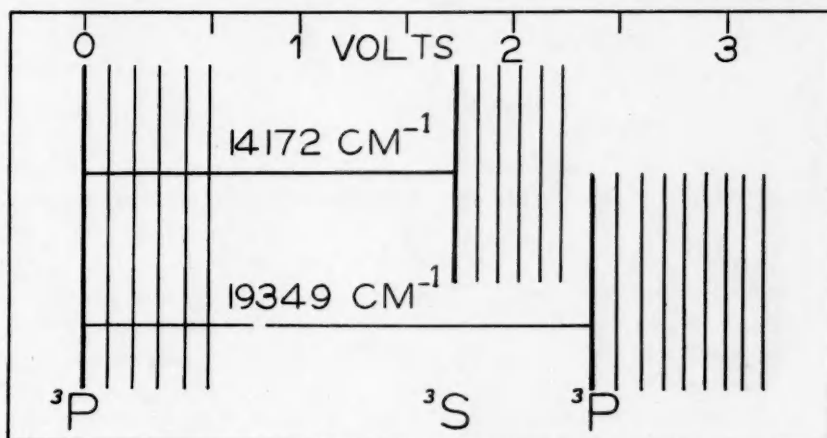
Fig. 1.—Known energy-levels of the *TiO* molecule

8 and 7 volts, respectively, for the energy possessed by the molecule
in the ^3S- and upper ^3P-state at the point of dissociation.

The calculated values of the heads for the o–2, 1–3, o–3, and
1–4 bands are given toward the end of Table I. Under favorable
conditions these four bands may appear, very weakly, in stellar
absorption spectra.

EQUILIBRIUM CONSTANT AND PARTIAL PRESSURES

One of the most interesting results which may be obtained when
the fine structure analysis and the heat of dissociation of a molecule
are known is the partial pressures of the various components which
enter into the chemical reaction. The process is somewhat similar
to that used by Saha[2] and others, in calculating the degree of ioniza-

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[1] *Ibid.*, **28**, 259, 1926.

[2] *Philosophical Magazine*, **40**, 472, 1920.

tion, or the partial pressures of the atom in its various excited states. The constant for the reaction $TiO \rightleftharpoons Ti+O$ may be defined as $K = P_{Ti}P_O/P_{TiO}$, where P is the partial pressure of the substance noted by the subscript. An equation connecting $\log P$ with the heat of dissociation, temperature, and other constants of the various components may be obtained from either statistical[1] or thermodynamic[2] considerations. The equation is

$$\log K = -5041 D/T + (5/2) \log T + (3/2) \log M + \log G - \log IT \\ + \log (1 - e^{-h\nu/kT}) - 39.688, \quad (5)$$

where

$K = P_{Ti}P_O/P_{TiO}$, the pressure in atmospheres

$D =$ Heat of dissociation in volts, in our case 6.74 volts

$T =$ Absolute temperature

$M = M_{Ti}M_O/M_{TiO}$, M being the masses of the components indicated in gram mols

$G = g_{Ti}g_O/g_{TiO}$, where $g = \Sigma(2j+1)$ for all levels of a multiplet

Since the lowest state of TiO is $^3P_{0, 1, 2}$, $j = 0, 1, 2$, $2j+1 = 1, 3, 5$, therefore $g_{TiO} = 1+3+5 = 9$. The lowest term of the oxygen atom is also $^3P_{2, 1, 0}$, therefore $g = 9$. For Ti, the lowest term is $^3F_{2, 3, 4}$, hence $g_{Ti} = 5+7+9 = 21$

$I =$ Moment of inertia of the molecule, i.e., 51.89×10^{-40} g.cm^2

$\nu = \omega_{1/2}$ for the lowest ^3P-state of TiO. In our case for simplicity $\omega''_{1/2}$ was taken to be 1000 cm^{-1}

Equation (5) is far more accurate than its application would warrant. In the derivation of the foregoing equation a harmonic instead of an anharmonic oscillator was assumed for the molecule. This gives the term $\log (1 - e^{-h\nu/kT})$. It has been assumed also that there is no nuclear spin either in the separate atoms or in the molecule. The main uncertainty lies in the term containing D. A small error in this quantity will introduce a large error in K.

Inserting these values into Equation (5), we get

$$\log K = 33973.6/T + (3/2) \log T + \log (1 - e^{-1430/T}) + 1.902. \quad (6)$$

In Table II are given the values of $\log K$ and K for various temperatures from $T = 1400$ to $4000°$ abs.

[1] Gibson and Heitler, *Zeitschrift für Physik*, **49**, 465, 1928.

[2] The writer is indebted to Professor Giauque for suggestions on this point; Giauque and Wiebe, *Journal of American Chemical Society*, **50**, 101, 1928.

It is known that the *TiO* bands persist in stars up to temperatures of about 3300° T.[1] At this temperature $\log K = -2.9617$, hence $K = P_{Ti}P_O/P_{TiO} = 2.68 \times 10^{-3}$. Whether a band present in stellar spectra is observed or not depends upon the intensity of the band in question as well as upon the dispersion of the apparatus used. We may reasonably assume that with the instruments used in stellar spectroscopy the titanium bands will not be observable if the ratio of titanium to titanium monoxide is as 100 to 1. Hence, we have $P_o = 2.7 \times 10^{-6}$ atmospheres as the partial pressure of oxygen in the reversing layers. The order of magnitude of this value is probably

TABLE II

T (Abs.)	$\log K$	K	T (Abs.)	$\log K$	K
1400........	-17.8398	1.45×10^{-18}	1900.......	-10.3387	4.59×10^{-11}
1450........	16.9879	1.03×10^{-17}	2000.......	9.4229	3.77×10^{-10}
1500........	16.1854	6.53×10^{-17}	2200.......	8.8475	1.42×10^{-9}
1550........	15.4617	3.45×10^{-16}	2400.......	7.5249	2.98×10^{-8}
1600........	14.7549	1.76×10^{-15}	2600.......	6.4160	3.83×10^{-7}
1650........	14.0076	8.00×10^{-15}	2800.......	5.4592	3.47×10^{-6}
1700........	13.4799	3.32×10^{-14}	3000.......	4.6257	2.37×10^{-5}
1750........	12.8990	1.26×10^{-13}	3300.......	3.5718	2.68×10^{-4}
1800........	12.2520	5.59×10^{-13}	3500.......	2.9617	1.09×10^{-3}
1850........	-11.8314	1.47×10^{-12}	4000.......	-1.7079	1.96×10^{-2}

correct. From this value estimates may be made as to the partial pressures of *Ti* and *TiO*.

It has been assumed in the foregoing calculations that a normal *TiO* molecule gives on dissociation two atoms, both of which are in the normal state. However, if the excitation potentials of the molecule and atoms are not very large, we must consider secondary reactions giving us molecules and atoms in the excited states. Titanium[2] has numerous low-excitation levels from 0.8 to 1.1 volts. It can be shown that at 3500° T about 15 per cent of all titanium atoms are in these states. This will have the effect of increasing the foregoing value of the partial pressure of oxygen.

After the quantum analysis given here had been completed, a

[1] The highest temperatures of stellar atmospheres in which *TiO* bands are present is about 3500° T. This, however, is the temperature of the photosphere; that of the atmosphere is from 5 to 10 per cent lower, or about 3300° T.

[2] H. N. Russell, *Astrophysical Journal*, **66**, 347, 1927.

letter appeared in *Nature*[1] by F. Lowater, dated March 28, in which she reported the finding of a new system of titanium bands. No data are given as to the wave-lengths of the heads, but the system is apparently the same as that outlined herein.

In conclusion the writer desires to express his indebtedness to Professor R. T. Birge for valuable advice, to Professors H. N. Russell and C. Shane for many helpful suggestions, and to Dr. A. S. King for plates furnished. The writer also wishes to thank Dr. P. W. Merrill for the prints which were essential to the success of the present work.

[1] **123**, 644, April 27, 1929.

ON THE COMPOSITION OF THE SUN'S ATMOSPHERE[1]

By HENRY NORRIS RUSSELL[2]

ABSTRACT

The *energy of binding* of an electron in different quantum states by *neutral* and *singly ionized* atoms is discussed with the aid of tables of the data at present available. The *structure of the spectra* is next considered, and *tables* of the *ionization potentials* and *the most persistent lines* are given. The *presence* and *absence* of the lines of different elements in the solar spectrum are then simply explained. The *excitation potential, E*, for the strongest lines in the observable part of the spectrum is the main factor. Almost all the elements for which this is small show in the sun. There are *very few solar lines* for which *E exceeds 5 volts;* the only strong ones are those of hydrogen.

The *abundance* of the various elements in the solar atmosphere is calculated with the aid of the calibration of Rowland's scale developed last year and of Unsöld's studies of certain important lines. The *numbers of atoms* in the more important energy states for each element are thus determined and found to decrease with increasing excitation, but a little more slowly than demanded by thermodynamic considerations.

The *level of ionization* in the solar atmosphere is such that atoms of *ionization potential 8.3 volts are 50 per cent ionized.*

Tables are given of the *relative abundance* of *fifty-six elements* and *six compounds.* These show that six of *the metallic elements, Na, Mg, Si, K, Ca,* and *Fe,* contribute 95 per cent of the whole mass. The whole number of metallic atoms above a square centimeter of the surface is 8×10^{20}. Eighty per cent of these are ionized. Their mean atomic weight is 32 and their total mass 42 mg/cm². The well-known difference between elements of *even* and *odd* atomic number is conspicuous—the former averaging *ten times as abundant* as the latter. The *heavy metals,* from *Ba* onward, are but little less abundant than those which follow *Sr,* and the hypothesis that the heaviest atoms sink below the photosphere is not confirmed. *The metals from Na to Zn, inclusive,* are *far more common* than the rest. The *compounds* are present in but small amounts, cyanogen being rarer than scandium. Most of those elements which *do not appear* in the solar spectrum should not show observable lines unless their abundance is much greater than is at all probable. There is a chance of finding faint lines of some additional rare earths and heavy metals, and perhaps of boron and phosphorus.

The *abundance of the non-metals,* and especially of hydrogen, is difficult to estimate from the few lines which are available. *Oxygen* appears to be about as abundant by weight as all the metals together. The abundance of *hydrogen* may be found with the aid of Menzel's observations of the flash spectrum. It is finally estimated that the *solar atmosphere contains 60 parts of hydrogen (by volume), 2 of helium, 2 of oxygen, 1 of metallic vapors, and 0.8 of free electrons,* practically all of which come from ionization of the metals. This great abundance of hydrogen helps to explain a number of previously puzzling astrophysical facts. The temperature of the reversing layer is finally estimated at 5600° and the pressure at its base as 0.005 atm.

A *letter from Professor Eddington* suggesting that the *departure from the thermodynamic equilibrium* noticed by Adams and the writer is due to a *deficiency* of the number of atoms in the higher excited states is quoted and discussed.

The hope that from the familiar qualitative spectrum analysis of the solar atmosphere a quantitative analysis might be developed

is of long standing. Recent developments in spectroscopy and astrophysics have turned the hope into a rational anticipation. The most precise method of investigation—the study of the detailed contours of individual lines—promises the most, but it will be some time before it can be applied to the multitude of lines available. In the meantime, a survey of the problem and a discussion of the existing evidence regarding the relative abundance of those elements which show lines in the solar spectrum, and of the significance of the "absence" of those which do not, may be in order.

I. THE IONIZATION POTENTIALS AND SPECTRA OF THE ELEMENTS

The manner in which the appearance of the arc and spark lines of a given element in earlier and later types of the sequence of stellar spectra is governed by the condition of ionization and excitation in the atmosphere of the stars is now familiar. The way in which the spectra and related properties of the atoms themselves vary with the atomic number is less widely known, and our discussion may well begin with a summary of the facts as at present understood.

The electrons in an atom, whether neutral or ionized, are bound in different states—a term now preferable to the old "orbits." The more firmly bound inner electrons which form parts of the completed groups or "shells" are of concern in the spectroscopy of X-rays, but not of ordinary light. The latter deals with the outer electrons and with the complex set of excited states into which one or more of them may be raised from their normal positions. When there is but one outer electron, the various energy-levels, or spectroscopic terms, in which the atom itself can exist are intimately correlated with the state of this electron and are not very numerous, and the spectrum is then simple. When there are several outer electrons, however, a single configuration of electronic states may give rise (by space quantization) to an almost bewildering number of different spectroscopic terms, and the spectra are very complicated. As the number of outer electrons approaches that required to form a complete "shell," Pauli's restriction principle comes into play and the spectra are again simpler. The brilliant and detailed success of Hund's theory in predicting the characteristics of the spectrum from the electronic configurations is well known.

The transitions between spectroscopic terms, which give rise to the various spectral lines, are of great variety, but the transitions in the electronic states within the atom which accompany them are much simpler and afford the clue to what would otherwise be a hopeless maze.[1]

1. *Observed energy of binding of electrons.*—We may therefore best approach the subject by a study of the energy of binding of an electron, in different atoms, into the same state—that is, into the state characterized by the same total and azimuthal quantum numbers, and denoted, in Bohr's notation, by the symbols 1_1, 2_1, 3_1,—; 2_2, 3_2, 4_2,—; 3_3, 4_3,—; 4_4,—, or more commonly at present by the equivalent notation 1s, 2s, 3s,—; 2p, 3p, 4p,—; 3d, 4d,—; 4f,—.

This energy of binding is given, so far as data are available,[2] in Table I for neutral, and in Table II for singly ionized atoms. The first column gives the atomic number; the next, the chemical symbol. The remaining columns give the energy in volts required to remove an electron in the given state from the atom, or liberated when it returns. Among the numerous energy-levels resulting from different space quantizations of the same electronic configuration, that with the greatest energy of binding is given, regardless of the multiplicity involved.

The lines across each column mark the completion of the shell of electrons in the state in question. For heavier elements, electrons of this sort belong to the interior of the atom. Their energy of binding increases rapidly but does not concern us here.

Most of the tabular values are derived from series in the spectra and are fully reliable. The rest have been estimated in different ways. Those in parentheses and given to two decimals are extrapolated by series formulae and should be substantially correct. Those in parentheses and with one decimal are interpolated between the corresponding entries for neighboring elements and may be in error by one- or two-tenths of a volt. Those in square brackets have been derived from these last with the aid of known lines and should be equally accurate. The numerous gaps represent terms

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[1] Cf., for example, "Related Lines in the Spectra of the Elements of the Iron Group," *Mt. Wilson Contr.*, No. 341; *Astrophysical Journal*, **66**, 184, 1927.

[2] References to the spectroscopic and other data are to be found at the end of the paper in Table XXI and in the list following this table.

TABLE I

ENERGY OF BINDING OF AN ELECTRON—NEUTRAL ATOMS

Z	El.	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p	5d
1	H	13.54	3.38	3.38	1.50	1.50	1.50	0.81	0.81	0.81	0.54	0.54	0.54
2	He	24.48	4.75	3.61	1.86	1.57	1.51	0.99	.87	.85	.61	.56	.54
3	Li		5.36	3.40	2.01	1.55	1.51	1.05	0.87	.85	.64	.55	.54
4	Be		9.29	6.57	2.86		1.62	1.32	1.19	.90	.76		.57
5	B			8.28	3.34	2.42	1.52	1.49	1.32	.87			.57
6	C			11.22	3.78	2.78	1.57		1.41	.87			
7	N			14.50	4.20	2.86	1.55	1.69	1.38	.86			.56
8	O			13.56	4.45	(3.0)	1.52	1.77	1.70	.86			.55
9	F			[17.3]	(4.7)	3.17			1.89	.85			
10	Ne			21.47	4.93	3.02	1.53	1.86	2.48	1.05	.93		.55
11	Na				5.11	4.92	1.51	1.94	[2.6]	1.15	.95	.80	.54
12	Mg				7.61	5.95	1.88	2.52	2.84	1.16	1.00	.79	.66
13	Al					8.14	1.95	2.83	2.72	1.06	1.02	.92	.75
14	Si					[10.5]		3.08		1.06	1.21	0.99	
15	P					10.31	(1.98)	(3.5)		0.94	1.31		.65
16	S					[12.9]	3.82	3.82		1.42	1.37		
17	Cl					15.69	(1.93)	(3.9)		1.66	(1.59)		.65
18	A						1.65	4.19		1.60	1.69	1.19	.59
19	K							6.09	4.21	1.64	1.72	1.29	.81
20	Ca							6.57	4.59	1.63	2.19	1.27	
21	Sc						3.57	6.80	4.76	1.65	2.40		
22	Ti						5.13	7.04	4.92	1.65	2.32		
23	V						5.95	7.28	5.05	1.66	2.35		
24	Cr						6.68	7.40	5.09	1.68	2.43		
25	Mn						8.24	7.83	5.45	1.87	2.54		
26	Fe						5.76	8.25	5.33		2.55		
27	Co						6.98	8.65	5.58		2.62		
28	Ni						8.63	9.02	5.30		2.55		
29	Cu						10.41	9.36			2.69		.89
30	Zn										2.72		0.94
31	Ga								5.98		2.92	1.57	1.04
32	Ge								7.89		3.26	1.80	
33	As								[9.6]		(3.4)	1.89	(0.8)
34	Se								[9.4]		(3.4)		
35	Br								[11.4]		(3.6)		
36	Kr								[13.9]	(1.9)	(3.9)		0.88
37	Rb									1.76	4.13	2.60	1.34
38	Sr									3.42	5.65	3.82	1.61
39	Yt									5.04	6.40	4.55	

TABLE II

Energy of Binding of an Electron—Singly Ionized Atoms

Z	El.	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p	5d
2	He^+	54.16	13.54	13.54	6.02	6.02	6.02	3.38	3.38	3.38	2.16	2.16	2.16
3	Li^+	(80.)	16.58	14.70	6.83	6.24	6.03	3.72	3.48	3.39	2.33	2.22	2.17
4	Be^+		18.13	14.18	7.25	6.27	6.03	3.88	3.47	3.40	2.41	2.21	2.17
5	B^+		23.	20.41	9.00	7.27	6.43	4.52		3.56			
6	C^+			24.28	9.90	8.01	6.31	4.87	4.22	3.52	2.85		2.24
7	N^+			29.50	11.10	8.93	6.45	5.22		3.54	3.04		
8	O^+			34.94	12.09	9.76	6.37	5.44			3.10		
9	F^+			[34.9]	(13.1)								
10	Ne^+			40.89	13.74	10.40	6.33	5.98	5.01	3.34	3.51	2.94	2.20
11	Na^+			47.02	14.31	10.83	6.20	6.18	5.73	5.15	3.92	3.22	3.34
12	Mg^+				14.97	10.56	6.13	6.33	6.25	3.80	4.18	3.44	2.40
13	Al^+				18.74	14.12	8.19	7.48	7.08	4.07	4.58		
14	Si^+					16.27	6.46	8.24	7.51	4.54	4.75		
15	P^+					19.81	6.95	9.11	7.98	4.79	5.08		
16	S^+					23.32	9.70	9.80	8.42	4.90	5.16		
17	Cl^+					[23.9]	10.25	10.56	9.07	5.43	5.08		
18	A^+					27.62	11.23	11.00	8.72	4.80	5.37	4.35	2.84
19	K^+					31.68	11.50	11.62	9.58	5.40	5.68		
20	Ca^+						10.14	11.82	9.98	5.55	5.90		
21	Sc^+						12.19	12.80					
22	Ti^+						13.45	13.60	(10.3)	5.85	6.50		
23	V^+						(14.7)	(14.4)	(10.7)				
24	Cr^+						(16.6)	(15.1)	10.91	5.85	6.50		
25	Mn^+						13.93	15.70	(11.7)				
26	Fe^+						(16.3)	(16.5)	(11.7)				
27	Co^+						(17.2)	(16.8)	11.75				
28	Ni^+						18.19	17.62	12.13				
29	Cu^+						20.34	17.15	11.79	5.92	7.20	5.40	3.35
30	Zn^+							17.89	14.00	5.68	6.99		
31	Ga^+							17.89	14.00	5.68	7.14	5.40	
32	Ge^+							(18.8)	15.98	6.00	8.28	6.21	3.62

which have not yet been identified spectroscopically—often because they would give lines in the infra-red. For the elements beyond yttrium the data are too fragmentary to tabulate.

The 4f state is not included in the table because it gives few terms of spectroscopic importance for the elements here considered.

It will be noticed that the rows in the table are filled out to the end only for the elements in which a shell of electrons is completed and for those immediately following. In these cases the spectra are relatively simple, and long series have been observed. For elements in which a group is about half complete (such as iron), the recognizable electronic configurations are few, although the number of spectroscopic states and of spectral lines is very great.

Table II is arranged the same as Table I. It stops at Ge^+ for lack of data. A number of the entries have been derived by interpolation or extrapolation in different ways. Some of them may be in error by half a volt; that for Li^+, by 3 or 4 volts.

The data of these tables are plotted in Figures 1 and 2, which illustrate many important atomic properties. The most firmly bound states are represented by the lowest points. The s, p, and d states are plotted as circles, crosses, and dots, respectively, and corresponding states in different atoms are connected by lines to guide the eye. These lines terminate abruptly at the points corresponding to the filling of a complete shell of electrons in the state considered. For larger atomic numbers these electrons pass into the inner structure, and those corresponding to the next lowest line on the diagram take their place as outer electrons. Thus a shell of six 2p electrons is filled up from B to Ne (or from C^+ to Na^+ among the ions). A shell of two 3s electrons is then filled in Na and Mg, followed by one of six 3p electrons (Al to A). Two 4s electrons go on in K and Ca, followed by ten 3d's from Sc to Zn. In this case, the 4s and 3d electrons are bound with about equal firmness and both groups are to be considered as outer electrons until the two shells are completely filled. Similar conditions are met from Yt to Cd (just beyond the limits of the diagram), where 5s and 4d electrons are going on, and among the rare earths (6s, 5d, and 4f). All this is, of course, merely a graphical representation of Bohr's theory of atomic structure.
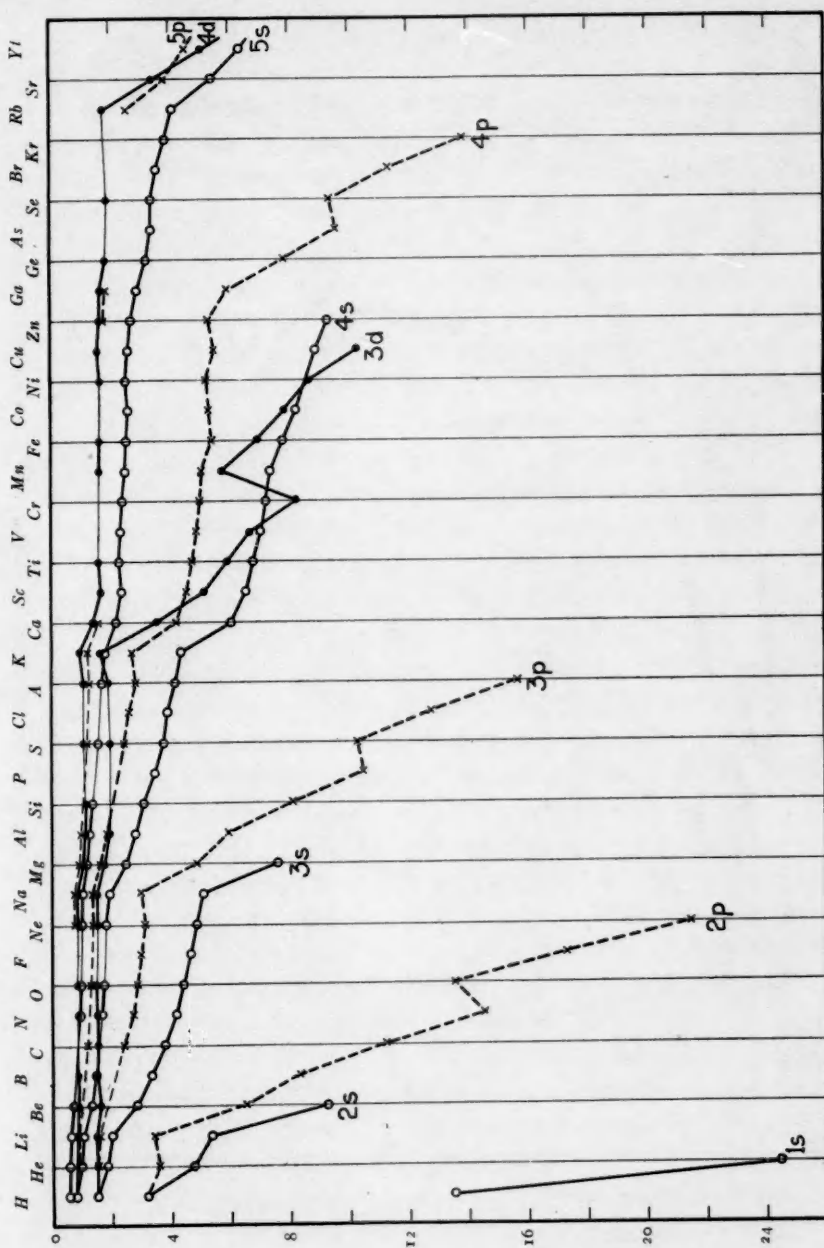
FIG. 1.—Energy of binding of electrons: neutral atoms
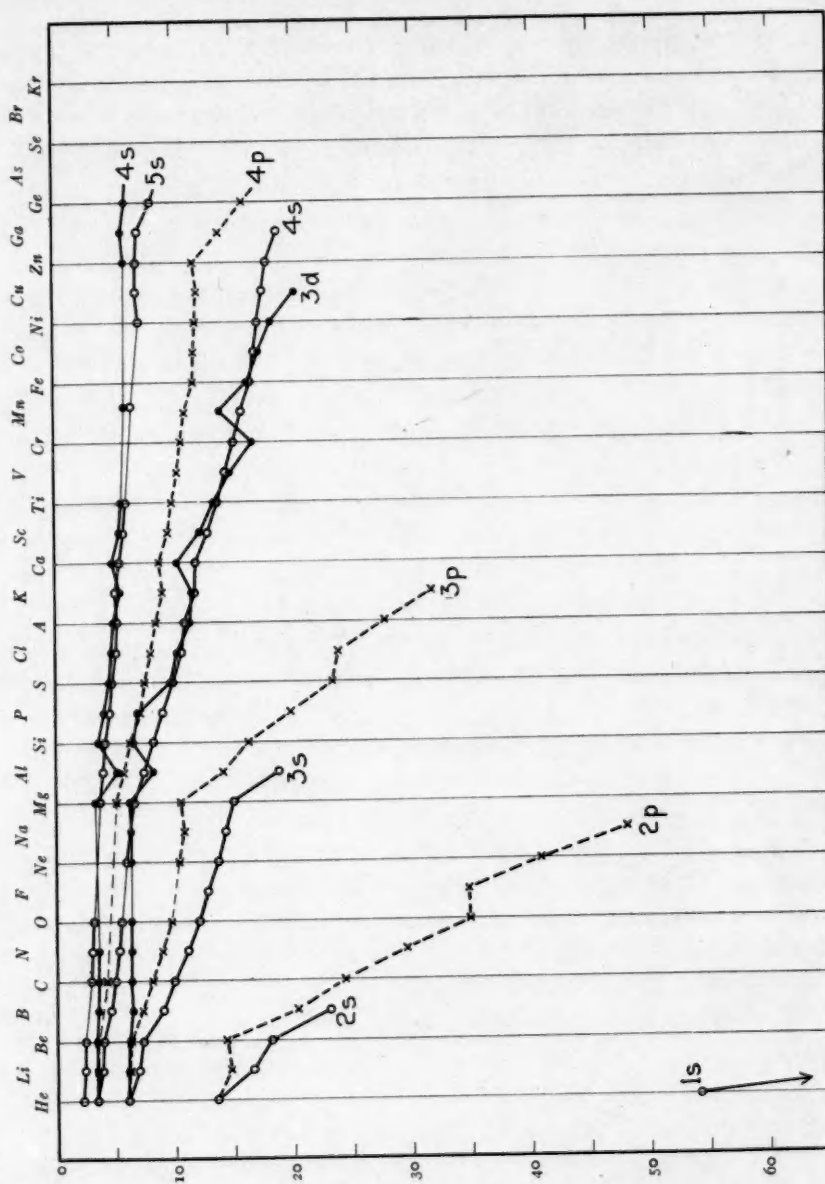
FIG. 2.—Energy of binding of electrons: singly ionized atoms

Among the relations which are illustrated by these figures we may note:

a) The diagrams for the neutral and ionized atoms are strikingly similar, not only in their general outlines, but also in detail. In other words, the familiar "displacement law" applies not only to the multiplicities present in a spectrum, but also to the energy relations —the spark spectrum of any element resembling in both respects that of the arc spectrum of the preceding element. The further remarks apply therefore to both arc and spark spectra.

b) The energy of binding, for an electron in a given state, increases with the atomic number. For the s states the increase is steady; for the p and d states it is interrupted by fluctuations, which are remarkably similar in the neutral and ionized atoms.

c) The increase of energy is most rapid (1) when electrons of the type considered are being added to build up a complete shell; (2) when s electrons are being added. The most conspicuous fluctuations occur when a shell is half completed (half of the 6 p electrons in N, P, As, O^+, S^+, and of the 10d electrons in Cr, Mn^+).

The explanation of these regularities by the older orbit theory is very pretty. For an outer excited orbit the increase in nuclear charge with atomic number is nearly compensated by the screening action of the electrons circulating in smaller orbits near the nucleus, and the effective attraction and energy of binding increase but slowly until electrons in orbits of the same type begin to be added, when the screening becomes very imperfect and the binding energy rapidly rises. The s orbits come nearer the nucleus than the others; hence they are less screened, and have greater binding energy than p orbits of the same total quantum number—and these again less than d orbits. Moreover, they go farther from the center; hence screening by an s electron is less effective and the binding energies of all outer orbits increase when they are being built in. Finally, the irregularities in the p and d curves can be explained as effects of space quantization. The conspicuous breaks which occur when a shell is half built are interpreted as due to the change from magnetic attraction to repulsion, when Pauli's restriction first compels the added electron to have a direction of spin opposite to that of the electrons which are already present.

The wave theory, when developed to include these complicated cases, will doubtless give a still better, though less picturesque, account of the facts. But we must return to spectroscopic considerations.

2. *Characteristics of the spectra of different elements.*—It may now be recalled that spectral lines are emitted, or absorbed, when an atom changes from one energy-level to another. Since the standpoint of the present paper is astrophysical, we may think of lines primarily as arising from transitions from lower to higher energy-levels, with absorption of radiation.

Whether such a transition will ordinarily occur, or is "forbidden," depends on the nature of the electronic transition involved. In permissible transitions one electron must jump between an even state (s or d) and an odd one (p or f). Another may jump at the same time between two even or two odd states, but this need not concern us for the moment.

Actual lines will therefore be represented in our diagrams by transitions between a point on a continuous line and one on a dotted line, while those between points on lines of the same sort are forbidden. When it is further recalled that the wave number of the line is proportional to the energy change involved, i.e., to the vertical shift on the diagram, some of the most important properties of the spectra and their variation with atomic number may be read from the figures. The wave-length of any line and the corresponding energy change in volts are related by the equation $\lambda = 12,336/V$. Taking sodium as an example, we see from Figure 1, or Table I, that an atom in the lowest energy state 3s can undergo transitions to 3p, 4p, 5p, etc., absorbing energy equivalent to 2.09, 3.73, and 4.32 volts, and giving lines at $\lambda\lambda$ 5900, 3310, and 2860 which agree, within the errors imposed by neglected decimals, with the lines of the principal series at $\lambda\lambda$ 5896, 3303, and 2853. An atom in the 3p state may change to 4s, 5s, absorbing 1.08, 2.00 volts ($\lambda\lambda$ 11404, 6160), or to 3d, 4d (1.51, 2.17 volts, $\lambda\lambda$ 8194, 5688). Changes between the higher states give lines in the infra-red.

The spectrum of sodium therefore shows strong lines in the easily accessible region. It is evident from inspection of Figure 1 that the same will be true of magnesium. For aluminium the 3s configura-

tion has gone inside the atom, and the principal jumps between the remaining states, 3p to 4s and 3d, are longer, so that the lines are in the violet and ultra-violet. For the following elements, from silicon to argon, these transitions increase in energy and the lines move into the far ultra-violet and the Schumann region, while the transitions next in importance, 4s to 4p, are still of small energy, and give lines in the infra-red, or beyond sulphur, in the deep red. Those from 4s to 5p give accessible lines which shift from the yellow for silicon to the violet for argon; but these lines, as is true in general for the later members of series, are relatively faint. In the case of phosphorus, indeed, they have not yet been recognized, nor have the infra-red lines arising from the transition 4s − 4p been observed. The arc spectrum of phosphorus, then, contains no known lines except in the ultra-violet beyond λ 2500, and it is obvious why it has not been recognized in the sun.

Similar conditions are encountered for all the non-metallic elements, which, with the exception of hydrogen and helium, belong where an outer shell of p electrons is being built up. The transition from the lowest configuration, mp, to the next, (m+1)s, gives lines in the far ultra-violet; the next, from (m+1)s to (m+1)p, lines in the deep red or infra-red, and only the weak lines, (m+1)s to (m+2)p, are accessible. For hydrogen and helium the energy relations are similar, except that $H\alpha$ is visible.

It must further be borne in mind that even at solar temperatures the great majority of the atoms of any given kind, whether ionized or neutral, will be in the state of lowest energy. The number in higher states decreases rapidly as the energy of excitation increases. The fraction of the atoms of a non-metal which are in the excited s state and capable of absorbing the infra-red or visible lines, is, therefore, small. This imposes an additional handicap upon the non-metals, and it is no wonder that they show so feebly in the sun.

Silicon is an exception. To understand its case we must remember that Figure 1 is a mere skeleton. Except when the formation of a new shell is just beginning, as in *Na* or *Al*, there are a number (often a great number) of additional atomic states, which correspond to the same electron configuration, with different space quantization. Such states would be represented on the figure by a swarm of

other points, lying above those which have been plotted by amounts ranging from a fraction of a volt to 2 volts or more. Those which belong to the same electronic configuration as the lowest state are metastable. In silicon there are two metastable states belonging to the configuration here called 3p. One of them is 0.78 volt above the bottom, and its combination with the 4s levels gives only wave-lengths shorter than λ 3000. The other, which is 1.12 volts higher, combines with the same levels to give the lines at λλ 3905 and 4102, which are strong in the sun. From phosphorus to argon, however, the corresponding lines are beyond λ 3000 and inaccessible astro-physically.

One non-metal, however, presents a real and glaring exception to the general rule. The hydrogen lines of the Balmer series, and, as Babcock has recently shown,[1] of the Paschen series as well, are very strong in the sun, though the energy required to put an atom into condition to absorb these series is, respectively, 10.16 and 12.04 volts—higher than for any other solar absorption lines. The obvious explanation—that hydrogen is far more abundant than the other elements—appears to be the only one.

Among the metals of the first long period, from scandium to zinc, the number of these additional energy states is great. The metastable states are numerous, since both 4s and 3d electrons may take part in forming them, and there are many higher states which are not represented at all in Table I or Figure 1. The tabular data give the energy released when an electron in the various states is added to ionized atoms which are in the states tabulated under 4s in Table II and described in a more generalized notation by $d^{n-2}s$. Addition of similar electrons to the ions in the states tabulated under 3d (in the general notation d^{n-1}) gives an entirely different set of higher energy-levels. Combinations between terms belonging to the two families, although usually involving a double electron jump, are very common, and add much to the complexity of the observed spectra. The tabular data, though referring to only a single family, give, however, a very good idea of the positions of the stronger lines. For each of the metastable spectroscopic terms there is a certain family of higher terms which arise from the addition of an electron

[1] *Revision of Rowland's Preliminary Table of Solar Wave-Lengths*, p. 223.

to the same metastable state of the ion, and have this state as their series limit. Combinations between terms of the same family give, in general, much stronger lines than those between terms of different families. Hence these strong lines, when arising from the same electronic transition, lie usually in much the same part of the spectrum for all the families.[1]

A glance at Figure 1 shows that among the elements considered the transition from 4s to 4p involves an energy change which increases slowly and rather steadily from 1.8 volts for *Ca* to 4.1 for *Zn*. The corresponding lines work from the red into the near ultra-violet as the atomic number increases. The energy of transition from 4p to 5s increases, though more slowly, from 2.0 to 2.4 volts, giving lines in the visible spectrum. The spectra of the metals of the "iron group" contain therefore strong lines (usually very numerous), which correspond to electron transitions from the low to the middle terms (4s — 4p or 3d — 4p). These lie mainly in the visible spectrum for the smaller atomic numbers, but shift into the ultra-violet toward the end of the group, until, in *Cu* and *Zn*, very few are left on the red side of λ 3000. They are low-temperature lines in the furnace. The transitions from the middle to the higher levels, 4p — 5s or 4p — 4d, give high-temperature lines in the laboratory which remain in the visible spectrum throughout the group. They overlap the low-temperature lines widely, but, on the whole, have shorter wave-lengths—which explains the well-known fact that arc lines in the red are in general harder to produce by temperature excitation than those in the violet.

The next six elements, in which 4p electrons are successively added, are very like the 3p group. Germanium, like silicon, has a few low-temperature lines in the visible region; arsenic, like phosphorus, has none at all so far as present observations go; and the rest could be detected only by faint lines demanding high excitation. The spark spectra behave very similarly, except that the energy steps are much greater and the lines much farther to the violet. The transitions from the low terms to middle terms belonging to the same family give the strongest enhanced lines, which are prominent

[1] For an example in *Ti* II, see *Mt. Wilson Contr.*, No. 344; *Astrophysical Journal*, **66**, 323, 1927.

in the arc spectrum also. These lines lie in the violet for the metals at the beginning of a group, Ca^+ and Sr^+, but shift rather fast toward shorter wave-lengths, so that, beyond V^+ and Cb^+, they pass into the closed region beyond λ 3000. Weaker lines, produced by transitions between the upper levels of the "low" group and the lower levels of the middle group, belonging to different families, are observable as far as Fe^+, and a few for Co^+ and Ni^+, after which they, too, are lost in atmospheric absorption. Such lines are usually faint in arc spectra. Transitions from the middle to the upper terms give lines which, in the laboratory, are practically confined to the spark. Among the metals these transitions involve more energy than those previously considered, and the corresponding lines are observable only at the beginning of a group (Ca^+ to Ti^+, and homologous elements). An especially interesting case is that of Mg^+, where 3s — 3p, 3p — 4s, and 3p — 3d give lines lying near together ($\lambda\lambda$ 2795, 2936, 2798) and all just out of reach, so that the observable lines correspond to high excitations, such as 3d — 4f (λ 4481). For Be^+, however, the principal pair is just accessible at λ 3131.

For the non-metals, the principal enhanced lines are hopelessly far out, and only a few transitions between highly excited states are accessible. The only enhanced lines of a non-metal which have been observed in the sun are a few of Si^+; and for these, as Figure 2 shows, the excitation potential is less than in almost any other case. The enhanced lines of the alkali metals present the same situation in its most extreme form.

3. *Ionization potentials.*—In discussing the relative strength of arc and enhanced lines in any source, knowledge of the ionization potentials involved is essential. These are given in Tables III and IV. Their values, for the first thirty-nine elements, are implicitly contained in Tables I and II—but not quite obviously. What is required in most cases is the energy difference between the normal states of the neutral atom and the ion, and complications arise in the iron group. Table I gives the energy difference between the 4s state of the ion ($d^{n-2}s$) and the various states of the neutral atom, of which we must evidently choose the lowest, whether it be 4s ($d^{n-2}s^2$) or 3d($d^{n-1}s$). But sometimes, as Table II shows, the 3d (d^{n-1}) state

of the ion is the lowest, and the values of Table I must be corrected accordingly. This is taken into account in Table III. For the second ionization potentials (Table IV) no such complication occurs. Both tables have been extended to include those heavier elements for which data are available. They are divided into two sections, corresponding to the "building on" of shells of s and d, or of p electrons. *He*, *Be*, *Mg* are put on the line with *Zn*, *Cd*, *Hg* because their spectra resemble those of the latter much more closely than those of *Ca*, *Sr*, and *Ba*. The line below *La* marks the position of the rare earths, where fourteen 4f electrons are added. These elements are listed separately.

The changes in ionization potential from element to element are immediately comprehensible by reference to Figures 1 and 2. While each shell of outer electrons is being completed, it increases, although with minor irregularities due to space quantization or to the interchange of s and d configurations. It reaches a maximum whenever a shell is completed. The drop after completion of an s shell in *Be* and *Mg* is between 1 and 2 volts; after completion of the combined s and d shells in *Zn*, *Cd*, *Hg*, it is 3 or 4 volts, while that following the completion of a p shell in the inert gases is much greater— 8 to 16 volts. For the second ionization, these discontinuities are greater in absolute value, but are a smaller fraction of the potentials themselves. The ratio of the first and second ionization potentials for similar electronic structures—that is, for the neutral atom of one and the ion of the next following—ranges from 2.9 to 2.5 when a group of electrons begins to be formed, while for atoms with completed groups it runs from 2.4 to 2.0. For the first few elements, it has higher values, culminating with 4.0 for H and He^+.

The general character of the spectra of most of the heavier elements can be deduced from Tables III and IV. For the second long period (Rb to Xe) the ionization potentials are nearly the same as for homologous elements in the first, but average a little lower. The same is true, in general, regarding the other energy-levels, so that the arc and spark spectra of these elements show high- and low-excitation lines in the same regions of the spectrum as for those of the first long period, but, on the whole, a little farther to the red.

At the beginning of the next period, we find the lowest known

TABLE III

First Ionization Potentials of the Elements

H 13.59																	He 24.48
Li 5.36	Be 9.29											B 8.28	C 11.22	N 14.50	O 13.56	F [17.3]	Ne 21.47
Na 5.11	Mg 7.61											Al 5.95	Si 8.14	P [10.5]	S 10.31	Cl [12.8]	A 15.69
K 4.33	Ca 6.09	Sc 6.57	Ti 6.80	V 6.76	Cr 6.74	Mn 7.40	Fe 7.83	Co 7.81	Ni 7.64	Cu 7.69	Zn 9.36	Ga 5.98	Ge 7.89	As [9.6]	Se [9.4]	Br [11.4]	Kr [13.9]
Rb 4.13	Sr 5.65	Yt 6.5	Zr	Cb	Mo 7.35	Ma	Ru 7.7	Rh 7.7	Pd 8.28	Ag 7.33	Cd 8.95	In 5.76	Sn 7.37	Sb 8.35	Te [8.7]	I [10.2]	Xe [12.1]
Cs 3.86	Ba 5.19	La 5.5	Hf	Ta	W 8.1	Re	Os	Ir	Pt 9.2	Au 9.20	Hg 10.39	Tl 6.08	Pb 7.38	Bi 7.25	Po		Rn ....

Ce	Pr	Nd	Il	Sa	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
6.9	5.8	6.3	....	6.6	....	6.7	6.7	6.8	....	....	....	7.1	....

TABLE IV

Second Ionization Potentials

Light elements

He^+ 54.16							
Li^+ (80)	Be^+ 18.13	B^+ (23)	C^+ 24.28	N^+ 29.50	O^+ [34.9]	F^+ ·····	Ne^+ 40.89
Na^+ 47.02	Mg^+ 14.97	Al^+ 18.74	Si^+ 16.27	P^+ 19.81	S^+ 23.32	Cl^+ [23.9]	A^+ 27.62
K^+ 31.68							

Long periods

Period 4	Period 5	Period 6	Period 7
Ca^+ 11.82	Sr^+ 10.98	Ba^+ 9.96	Ra^+ 10.2
Sc^+ 12.80	Yt^+ 12.3	La^+ ·····	Ac^+ ·····
Ti^+ 13.60	Zr^+ ·····	Hf^+ ·····	Th^+ ·····
V^+ (14.7)	Cb^+ ·····	Ta^+ ·····	Pa^+ ·····
Cr^+ (16.6)	Mo^+ ·····	W^+ ·····	U^+ ·····
Mn^+ 15.70	Ma^+ ·····	Re^+ ·····	
Fe^+ (16.5)	Ru^+ ·····	Os^+ ·····	
Co^+ (17.2)	Rh^+ ·····	Ir^+ ·····	
Ni^+ 18.19	Pd^+ 19.8	Pt^+ 18.9	
Cu^+ 20.34	Ag^+ 21.9	Au^+ 20.0	
Zn^+ 17.89	Cd^+ 16.82	Hg^+ ·····	
Ga^+ (18.8)	In^+ ·····	Tl^+ ·····	
Ge^+ 15.98	Sn^+ 14.5	Pb^+ 14.96	
As^+ ·····	Sb^+ ·····	Bi^+ ·····	
Se^+ ·····	Te^+ ·····	Po^+ ·····	
Br^+ ·····	I^+ ·····		
Kr^+ ·····	Xe^+ ·····	Rn^+ ·····	
Rb^+ 26.4	Cs^+ ·····		

ionization potentials (Cs, and Ba^+ for the second stage), which remain lower than in other periods until the rare-earth group begins. In these elements the outer electrons consist of two 6s, one 5d, and from one to fourteen 4f electrons, and it is reasonable to suppose that the ionization potential slowly rises as the 4f group is built up. For the earlier members of the group, the lines of the ionized atom are the main features of the arc spectrum and those of the neutral atom are best brought out in the furnace, thus showing that the first ionization potentials are very low.[1] The strong lines of the first spark spectrum shift toward the violet with increasing atomic numbers, which practically proves that the second ionization potential, at least, increases. For the later members of the group, one would expect the ionization potential to be high enough to make the lines of the neutral, rather than the ionized, atom conspicuous in the arc—but the necessary spectroscopic data are lacking. The number of atomic energy states should be much greater among the rare earths than for any other elements, and their spectra are actually very intricate.

Upon the completion of the shell of 4f electrons it ceases to have any important effect on the properties of the elements, as is shown by their chemical behavior and what little is known of their spectra (Hf^+, W). We should therefore expect a considerable fall in the ionization potential between the last rare earth, Lu, and Hf, and then a gradual rise to Au and Hg. For the last-named elements ionization is more difficult than for the homologous elements in the preceding periods. Whether this is also true for Hf cannot be determined from the existing data.[2]

4. *Raies ultimes.*—The strongest lines of any element, which are the last to disappear when the quantity present is diminished, usually arise from transitions from the lowest energy-level to middle levels of the same multiplicity and belonging to the same family. Among the various lines in a multiplet, that involving the highest inner quantum numbers is the most persistent; among transitions

[1] The measures of Rolla and Piccardi indicate that it reaches about 7.5 volts at the end of the group.

[2] A table of ionization potentials, with discussion, has been given by Rolla and Piccardi (*Philosophical Magazine*, **7**, 286, 1929).

to terms of the same family the term of greatest azimuthal quantum number has the advantage; and the larger multiplicities are preferred to the smaller.[1] In a few cases, the combination of these influences causes a line originating from a level a little above the lowest to be the most persistent of all.

Lists of these lines, in the various arc spectra, are given in Table V. The lines marked with an asterisk have been recorded by De Gramont[2] or Meggers and Kiess[3] as *raies ultimes*, which actually persist in the manner described. Most of the rest are of too short wave-length to have been observed by them, but are undoubtedly of the same nature. Table VI gives similar data for spark spectra. The arrangement for the short periods differs slightly in order to bring spectroscopically similar terms into the same line.

These tables confirm the conclusions which were drawn from the general structure of the spectra. The most persistent arc lines of almost all the metals lie within the region accessible in the sun, while those of the non-metals are without exception out of range. Conditions for detecting the spark lines astrophysically are favorable only for the metals in the earlier parts of the successive periods—for *Be*, *Ca* to *V*, *Sr* to *Cb*, *Ba*, *La*, and probably several of the rare earths, and finally for *Ra*.

It may be remarked that the persistent lines and their spectroscopic notation are known for a number of elements for which the ionization potential and energy levels have not yet been determined. Indeed, the values given in square brackets in Tables I–IV have all been determined by utilizing persistent lines (not always the ones given in Tables V and VI), as explained in §1.

5. *Molecular spectra.*—No detailed discussion of the energy relations for the various band spectra which have been recognized in the sun is attempted here. It may be said, however, that, so far as the present evidence goes, all the bands which have been observed correspond to electronic transitions from the normal energy state of the molecule to higher states, and hence are comparable in nature to the persistent lines. Most of these bands are known to arise from mole-

[1] Laporte and Meggers, *Journal of the Optical Society of America*, **11**, 459, 1925.

[2] *Comptes rendus*, **171**, 1105, 1920.

[3] *Journal of the Optical Society of America*, **12**, 417, 1926.

TABLE V

Persistent Lines—Arc Spectra

Wave-lengths in I.A.

1	2	3	4	5	6	7	Classification
H 1215.7	Li *6707.85	Na *5895.93	K 7699.01	Rb 7947.64	Cs 8943.46		$^2S_1-^2P_2$
He 584.4	Be 2348.63	Mg *2852.11, 4571.10	Ca *4226.73	Sr *4607.34	Ba *5535.53	Ra 4825.9	$^1S_0-^1P_1$
			Sc 3911.81	Yt 4102.38	La	Ac	$^2D_3-^2F_4$
			Ti *3653.49	Zr *3601.18	Hf *4093.17†	Th	$^3F_1-^3G_5$
			V *4379.24	Cb *4058.99	Ta	Pa	$^6D_3-^6F_6$
			Cr *4254.34	Mo 3798.26	W 5053.30‡	U	$^7S_3-^7P_4$
			Mn 4030.76	Ma	Re		$^6S_3-^6P_4$
			Fe 3581.20	Ru *3498.95	Os		$^5F_5-^5G_6$
			Co *3465.80	Rh *3434.90	Ir *3220.79§		$^4F_5-^4G_6$
			Ni *3524.54	Pd *3404.09	Pt *3064.69		$^3D_3-^3P_2$
			Cu *3247.55	Ag *3280.66	Au *2427.98		$^2S_1-^2P_2$
			Zn 2138.61, 3075.88	Cd *2288.02, 3261.04	Hg *2536.52, 1849.57		$^1S_0-^3P_1$; $^1S_0-^3P_1$
	B *2497.7	Al *3961.54	Ga *4172.06	In *4511.27	Tl *5350.46		$^2P_2-^2S_1$
	C 1657.01, 1658.13	Si *2524.12, 2528.52	Ge 2709.63, 2754.59	Sn *2863.32, 3175.04	Pb 2833.07		$^3P_1-^3P_1'$; $^3P_2-^3P_1'$
	N 1200.7	P 1787.5	As 1972.0	Sb *2311.50	Bi *4057.83		$^4S_2'-^4P_1'$
	O 1302.25	S 1807.4	Se 1960.2	Te 2142.7	Po *3067.69		$^3P_2-^3S_1$
	F 954.7	Cl 1347.2	Br 1488.6	I 1642.5			$^2P_2-^2P_2'$
	Ne 735.8	A 1048.3	Kr 1164.9	Xe 1295.7	Rn		$^1S_0-^1P_1$

† Spectroscopic classification unknown (Meggers, *Bureau of Standards Journal of Research*, 1, 187, 1928).

‡ $^5D_1-^5P_2$. Excitation potential, 0.206 volts.

§ Spectroscopic classification unknown.

TABLE VI

PERSISTENT LINES — SPARK SPECTRA

WAVE-LENGTHS IN I.A.

Term	Period 1–2	Period 2	Period 3	Period 4	Period 5	Period 6	Period 7
$^2S_1-{}^2P_2$	He+ 303.8	Be+ *3130.42	Mg+ *2795.52	Ca+ *3933.66	Sr+ *4077.71	Ba+ *4554.04	Ra+ 3814.43
$^3D_3-{}^3F_4$				Sc+ *3613.84	Yt+ *3710.30	La+ *3949.10	Ac+ ….
$^4F_5-{}^4G_6$				Ti+ *3383.76	Zr+ *3391.96	Hf+ *2773.37†	Th+ ….
$^5F_5-{}^5G_6$				V+ *3093.10	Cb+ *3094.20	Ta+ ….	Pa+ ….
$^6D_5-{}^6F_6$				Cr+ *2835.64	Mo+ *2816.16	W+ ….	U+ ….
$^7S_3-{}^7P_4$				Mn+ *2576.12	Ma+ ….	Re+ ….	
$^6D_3-{}^6F_6$				Fe+ *2382.04	Ru+ ….	Os+ ….	
$^5F_3-{}^5G_6$				Co+ *2378.62	Rh+ ….	Ir+ ….	
$^4F_3-{}^4G_6$				Ni+ 2216.47	Pd+ ….	Pt+ 2296.53	
$^3D_3-{}^3P_2$				Cu+ 2247.00	Ag+ 2082.06	Au+ *2437.81	
$^2S_1-{}^2P_2$				Zn+ 2061.96	Cd+ 1942.3	Hg+ *2265.04	
$^1S_0-{}^1P_1$		B+ 1362.46	Al+ 1670.98	Ga+ 1414.4	In+ 1321.8	Tl+ 1586.4	
$^2P_2-{}^2S_1$		C+ 858.56	Si+ 1533.55	Ge+ 1649.27	Sn+ 1900.05	Pb+ *2203.5	
$^3P_2-{}^3D'_3$		N+ 1085.70	P+ 1542.29	As+ ….	Sb+ ….	Bi+ ….	
$^4S_2-{}^4P'_3$		O+ 834.46	S+ 1259.53	Se+ ….	Te+ ….	Po+ ….	
$^3P_2-{}^3P'_3$		F+ 656.81	Cl+ 1071.03	Br+ 886.29	I+ ….	….	
$^2P_2-{}^2P'_2$		Ne+ 460.72	A+ 919.69	Kr+ ….	Xe+ ….	Rn+ ….	
$^1S_0-{}^1P_1$	Li+ (192)‡	Na+ 376.34	K+ 612.61	Rb+ ….	Cs+ ….		

† See note for Hf in Table V.

‡ Not yet observed; estimated by extrapolation of series.

cules which are unsaturated chemically, and the others are probably of the same sort. For molecules which are stable enough to endure ordinary chemical manipulation, the normal energy state appears to be so far below the others that the bands absorbed by the unexcited molecules lie in the extreme ultra-violet and are inaccessible.

This is certainly true of the hydrogen molecules, and the presence of lines of the "secondary" hydrogen spectrum in sun-spots[1] which has just been reported would be as striking an exception to the general rule as is the great strength of the Balmer lines.

The sources from which the data regarding the spectra and ionization potentials of the elements have been taken are summarized in Table XXI at the end of the paper. It is hoped that the list of references following the table is fairly complete; but no attempt has been made at a general bibliography of the subject. In the cases marked by square brackets in the tables (and in a few others) this material has been further worked over by the writer.

II. THE PRESENCE AND ABSENCE OF THE ELEMENTS
IN THE SOLAR SPECTRUM

6. *Summary of the data.*—We are now in a position to understand the significance of the absence of recognizable lines of many of the elements from the solar spectrum. The present state of knowledge on this subject is summarized in Table VII, which is taken from the *Revision of Rowland's Table*,[2] with slight modifications, as explained below. The intensity of the strongest solar line which is believed to be due mainly, if not entirely, to the given elements is tabulated, thus indicating some idea of the prominence of the element in the spectrum, as well as its mere presence. The arc and spark spectra are tabulated separately under the headings El and El^+. An intensity given in parentheses signifies that the lines of the elements appear in spots, or in the disturbed regions near them, but not on the rest of the disk. A question mark shows that the identification of the element in the sun is uncertain. The table is arranged in fashion

[1] G. Piccardi, *Nature*, **122**, 880, 1928.

[2] *Carnegie Institution of Washington, Publication*, No. 396, 1928. Table A, p. xv. This will hereafter be referred to as R R. Since the publication of this work evidence has appeared that lines of *Pt* are probably, and *As* and *Ir* are possibly, present in the solar spectrum. This will be discussed in a forthcoming contribution by Dr. St. John.

TABLE VII

Intensities of Strongest Absorption Lines of Each Element in the Solar Spectrum

N	El	Int.	El+
1	H	40	—
2	He	(0)	.....
3	Li	(4)	.....
4	Be	-3	1
5	B	:	:
6	C	0	:
7	N	-2?	:
8	O	2	:
9	F	:	:
10	Ne	:	:
11	Na	30	.....
12	Mg	30	0
13	Al	20	-2?
14	Si	12	2
15	P	:	:
16	S	-1	:
17	Cl	:	:
18	A	:	:
19	K	5	.....
20	Ca	20	200
21	Sc	2	7
22	Ti	7	12
23	V	4	5
24	Cr	8	5
25	Mn	10	6
26	Fe	40	6
27	Co	6	0
28	Ni	20	2
29	Cu	10	:
30	Zn	3	:
31	Ga	-1	:
32	Ge	0	:
33	As	-3?	:
34	Se	:	:
35	Br	:	:
36	Kr	:	:
37	Rb	(1)	:
38	Sr	1	8
39	Yt	0	3
40	Zr	-1	2
41	Cb	-2?	-1
42	Mo	-2	0
43	Ma	|	|
44	Ru	-0	:
45	Rh	2	:
46	Pd	0	:
47	Ag	0	:
48	Cd	1	:
49	In	-1	:
50	Sn	0	:
51	Sb	-3?	:
52	Te	:	:
53	I	:	:
54	Xe	:	:
55	Cs	1	8
56	Ba	0	1
57	La	0	-1
72	Hf	-1	:
73	Ta	-2?	:
74	W	-2	:
75	Re	|	:
76	Os	-0	:
77	Ir	2	:
78	Pt	0	:
79	Au	0	:
80	Hg	1	:
81	Tl	(-1)	-2?
82	Pb	-2?	-2
83	Bi	-3	|
84	Po	:	|
85	—	:	|
86	Rn	:	:
87	—	:	|
88	Ra	:	|
89	Ac	:	|
90	Th	:	|
91	Pa	:	|
92	U	:	|
58	Ce	:	0 1?
59	Pr	:	-1 0
60	Nd	|	0
61	Il	:	1?
62	Sa	:	1?
63	Eu	:	0?
64	Gd	:	|
65	Tb	:	0?
66	Dy	:	|
67	Ho	:	1?
68	Er	:	|
69	Tu	:	1?
70	Yb	:	1?
71	Lu	:	|

similar to the others, except that the rare earths are added in a separate column.

The presence in the spectrum of the disk of band lines due to the molecules C_2, CH, CN, NH, and OH, and, in addition, of BO, MgH, CaH, TiO, and probably H_2, in the spot spectrum, should be mentioned for completeness and as affording the principal evidence for the presence of B, C, and N in the sun. The strength of the emission lines of He^+ in the chromosphere and the presence of a faint line of He^+ (λ 4685.808) are noteworthy.

It should further be borne in mind that some of the gaps in the table represent a lack of adequate data. The spectra of the recently discovered elements Ma and Re, and of the short-lived radioactive products, Po, Ac, and Pa, are still wholly or substantially unknown, and that of the "emanation" Rn is very incompletely observed. For several of the rare earths, Il, Tb, Ho, Tu, and Lu, the existing spectroscopic data "are not adequate either to establish the probability of their presence or to eliminate them from further consideration."[1] For these 11 elements, dashes have been inserted in the table to indicate the impossibility of a decision from existing data—as has also been done for the unknown elements of atomic numbers 85 and 87 and for the non-existent spark spectrum of hydrogen. This leaves 79 elements whose presence or absence in the spectrum can be discussed on the basis of existing data. Of these, 49 appear certainly to be present, 9 are doubtful, and 21 absent. Eighteen of the 49 reveal their presence by both their arc and spark spectra, 22 by the arc spectrum alone, 7 by the spark alone, and 2 (B and N) primarily by band spectra of compounds. Four of the doubtful identifications have to do with arc lines; the other 5 probably with spark lines (of the rare earths).

7. *Importance of excitation potential.*—In discussing this material, we may first consider the enhanced lines. Thirteen elements (Table VI) have their most persistent spark lines in the region accessible to observation. These are Be, Ca, Sc, Ti, V, Sr, Yt, Zr, Cb, Ba, La, Hf, and Ra. All but the last appear in the list of elements showing enhanced lines in the sun. Most of the other elements which do

[1] St. John and Moore, *Mt. Wilson Contr.*, No. 364; *Astrophysical Journal*, **68**, 106, 1928.

so (*Cr, Mn, Fe, Co, Ni, Mo*) come near the middle of the first two long periods. In their cases, the most persistent enhanced lines lie beyond λ 3000, but others, arising from low energy-levels, though not the lowest, are accessible. The rare earths should undoubtedly be divided between these two groups—just how cannot be said until the analysis of their spectra has been begun. The statement that enhanced lines are found in the sun for those elements which have lines of low excitation potential in the accessible region has therefore few exceptions. On the one hand, lines of *Ra*, and perhaps of some of the rarer of the rare earths, are absent. On the other, a very few enhanced lines, demanding high excitation, appear for *Mg* and *Si* and doubtfully for *Al*. It is obvious that considerations of abundance may explain both sets of exceptions. For the remaining elements which fail to show enhanced lines in the sun, the excitation potentials for the accessible lines are high in every case for which they have been determined.

The case of the arc spectra is not quite so simple. There are 37 elements, excluding the rare earths, whose arc spectra are little known, for which the most persistent lines are accessible. Arc lines of 25 of these are present in the solar spectrum. For 3 others (*Li, In, Rb*), the most persistent lines appear in sun-spots, though not on the disk. Three more (*Cb, Ir, Tl*) are doubtful, leaving 6 which fail to appear—*Cs, Ba, La, Hf, Bi*, and *Ra*. It is well known that most of these absences are explicable by ionization in the solar atmosphere.[1]

Among the elements whose most persistent lines are inaccessible, the majority of those which appear in the sun have accessible lines of low or moderate excitation potential (*Be, Mg, Si, Zn, Ge, Cd, Sb*, and the doubtful *As* and *Sn*). For the non-metals, *H, He, C, N, O*, and *S*, the excitation potentials are high and the lines weak, except for hydrogen.

It appears, therefore, that the principal factor which is unfavorable to the appearance of a spectral line in the sun is a high excitation potential. How important it is, is shown by Table VIII, which includes all the Fraunhofer lines which are known to have excitation potentials above 5 volts. There are 47 such lines out of nearly 6000

[1] M. N. Saha, *Philosophical Magazine* (6), **40**, 472 and 809, 1920.

for which the excitation potentials are known. Twenty-eight of them have intensity o or fainter, and only 1 exceeds intensity 2, except the hydrogen lines, whose altogether exceptional behavior is well illustrated.

Of the elements whose persistent lines appear in the sun, only a few (Fe, Cu, Co, Mn, Ca^+) show lines of high excitation, and the

TABLE VIII

SOLAR ABSORPTION LINES OF HIGH EXCITATION POTENTIAL

E.P.	El.	I.A.	Int.	E.P.	El.	I.A.	Int.
5.011....	Fe	8945.20	-1	7.455....	$C?$	9095.02	1
5.042....	Fe	8920.027	o		$C?$	9111.93	o
	Fe	9148.02	-1	7.473....	$Ca^+?$	5001.479	-2
5.064....	Fe	7086.729	-1	7.483....	$Ca^+?$	5021.153	-3
5.050....	Cu	4651.118	-1	7.591....	C	4932.020	-2
5.080....	$Cu?$	3319.689	-3		C	5039.006	-3
	$Cu?$	4586.998	-1	8.085....	Si^+	6347.104	2N
5.060....	Si	5948.552	6		Si^+	6371.362	1N
5.086....	Mg	7657.605	2	8.825....	Mg^+	4481.142	o
5.183....	$Co?$	6864.958	-3	8.826....	Mg^+	4481.340	o
5.467....	Mn	7680.267	1	9.106....	O	7771.954	2
5.771....	Zn	4629.806	-1		O	7774.177	2
	Zn	6362.357	1		O	7775.394	1
6.496....	$S?$	9228.19	-1	9.479....	O	8446.350	o
	$S?$	9237.49	o		O	8446.728	-1
6.827....	Si^+	3853.672	-1	10.155....	H	3970.078	5N
	Si^+	3862.595	1		H	4101.750	40N
6.829....	Si^+	3856.028	1		H	4340.477	20N
7.140....	$Mg?$	3892.017	-2		H	4861.344	30
7.388....	$Al^+?$	3900.662	-2		H	6562.816	40
7.450....	C	4770.001	-2	10.302....	$N?$	8680.403	-2
	C	4775.886	-2	12.035....	H	10049.5	25
	$C?$	9061.50	-1	20.871....	He	5875.62	*
	$C?$	9078.34	-1				

* Appears only in disturbed regions.

latter are all faint. The reason is simple: for such lines the lower level involved must be more than 5 volts above the bottom, and the upper level, even for a line at λ 8000, must be at a height of at least 6.5 volts. Aside from the case of a few exceptional states of low statistical probability, this level, again, will be well below ionization. Hence the ionization potential must be fairly high, as it is for the elements whose arc lines appear.

For spark spectra, the explanation is different. In order that the persistent lines may be accessible, the energy differences between the low and middle states (e.g., 4s, 3d, and 4p) must be rather small

compared with the energy of ionization. The differences between the levels next in series (e.g., 5s, 4d, and 5p) will then be so small that the corresponding lines are in the infra-red, and the only accessible lines of high excitation will be later members of series, which are inherently faint. An example is found in Ca^+, where the observed lines correspond to the electron transition 5p — 6d.

8. *Significance of the "absences."*—The excitation potentials for the accessible lines of those elements which have not been identified in the solar spectrum are given in Table IX, those for which no reliable spectroscopic data exist being omitted as usual. The last column contains the elements whose presence is doubtful.

TABLE IX

EXCITATION POTENTIALS FOR ACCESSIBLE LINES OF ELEMENTS WHICH ARE MISSING OR DOUBTFUL IN THE SOLAR SPECTRUM

El.	E.P.	El.	E.P.	El.	E.P.	El.	E.P.
B........	4.94	Kr.......	9.9	Au......	4.60	N.......	10.30
F........	12.62	Te.......	5.45	Hg......	4.65	S.......	6.50
Ne.......	16.54	I........	6.73	Bi......	0.00	As.......	2.30
P........	6.90	Xe.......	8.2	Bi$^+$......	>6	Sn.......	0.21
Cl.......	8.88	Cs.......	0.00	Ra......	0.00	Ir.......	0.35
A........	11.50	Cs$^+$.....	15.	Ra$^+$.....	0.00	Tl.......	0.00
Se.......	5.94	Ta.......	0. ?	Th......	0. ?		
Br.......	7.81	Os.......	0.00?	U.......	0. ?		

The values given to two decimal places are derived from known resonance lines and are accurate. Those given to one decimal involve estimates of the positions of levels near those given by resonance lines, but slightly lower, and should be correct to 0.1 volt. The remaining values require explanation. For *Os*, lines from the lowest level revealed by the present incomplete analysis are accessible; there may, however, be unrecognized levels which are still lower, but by no great amount.

The spectra of *Ta*, *Th*, and *U* have not been analyzed, but comparison with homologous elements makes it very probable that their persistent lines lie in the observable region. For *Bi$^+$* all that can be said is that the resonance lines are pretty certainly of shorter wave-length than for *Pb$^+$* (for which the E.P. is 6 volts). In the case of *Cs$^+$*, which has a spectrum similar to that of *Xe*, the energy

of binding of the 5p electron—the lowest state—may be estimated from the run of similar ratios for other elements, as 1.8 times the value for Kr I, that is, about 22 volts. The next level above this involves a 6s electron, which has a binding energy of 7.45 volts in Ba^+ and should have slightly less in Cs^+. The difference gives the tabular value of 15 volts. This may be wrong by a volt or two, but must be of the right order. For B, P, Te, Br, and I, lines of the given excitation potentials ought theoretically to exist in the infra-red, with fainter ones in the visible region; but none of these has yet been identified.

The elements which fail to appear in the sun fall sharply into two groups. The first contains all those with atomic numbers up to 54, Xe. Here the excitation potentials are so high that there is no chance of the lines appearing unless the elements are abundant. The same is true, to a somewhat less degree, of Au and Hg; and Cs may be added to the list for the reason that its first ionization potential is so low that no neutral atoms remain, even above the spots, and its second is so high that the observable lines demand a prohibitive degree of excitation. The absence of lines of these elements from the sun is consistent with their presence in fairly considerable amounts in the solar atmosphere.

The case of most of the heavier elements is quite different. For three of them—Os, Bi, and Ra—persistent lines lie in accessible regions and are definitely absent from the solar spectrum. Though Ra is probably easily ionized, the persistent lines of Ra^+ are also absent. There seems to be no escape, therefore, from the conclusion that these elements are present in the sun's atmosphere in negligible quantities, if at all.

For Ta, Th, and U, the spectra are complex, with numerous lines of moderate intensity and few very strong ones, and have not yet been analyzed. A definite decision upon their presence in the sun demands laboratory observations with the under-water spark, or some similar source, which will pick out the persistent lines among the swarms which fill the spectrum.

The weakness or absence of solar lines of the heavy metals is an old story. The present discussion indicates that this is not to be accounted for by the structure of their spectra (except for Au and

Hg) and supports the conclusion that these elements are present in the reversing layer in small proportions.

III. THE ABUNDANCE OF THE ELEMENTS IN THE SUN

9. *Absolute calibration of Rowland's intensity scale.*—There is reason to hope that within a few years the quantitative analysis of the solar atmosphere will be put on a solid basis by the accurate measurement of the contours of large numbers of lines and the interpretation of these by physical theory. An admirable beginning has already been made by Unsöld[1] and others; but a general investigation will be a heavy piece of work observationally, and perhaps theoretically too, and will take a long time to finish.

In the meantime a reconnaissance of the field may be made with the aid of the calibration of Rowland's intensity scale.[2] As derived last year, this gives only the relative numbers of atoms engaged in the production of different lines. More precisely, the numbers are those of the "fictitious oscillators," acting independently for each wave-length, which would produce lines of the observed intensity. For each spectral region the number of such resonators required to produce a line of intensity o was taken as the unit, irrespective of its absolute value or its possible variation in different regions.

Both these last questions may be approximately answered by comparison with Unsöld's results. From the observed contours of a number of typical resonance lines he determines theoretically the number of atoms, NH, above 1 sq.cm of the sun's surface, which are concerned in their production. When multiplied by a factor f, depending on quantum numbers, these give the number of "oscillators" for each line. The calibration of Rowland's table gives a quantity N, defined by the equation

$$\log N = B \log A , \qquad (1)$$

where B and $\log A$ are taken from empirical tables, which should be proportional to the number of oscillators. We may therefore write

$$\log (NHf) = \log N_0 + B \log A , \qquad (2)$$

[1] *Zeitschrift für Physik*, **46**, 765, 1928.

[2] Russell, Adams, and Moore, *Mt. Wilson Contr.*, No. 358; *Astrophysical Journal*, **8** 1, 1928.

where N_0 is the number of oscillators for a line of intensity o. Each of Unsöld's lines then gives a determination of N_0. The results are as shown in Table X, in which R denotes Rowland's intensity, "Res." the differences of the individual determinations of N_0 from the mean, and R_c the Rowland intensity computed from Unsöld's data by working the equations backward with the mean value of log N_0. The H and K lines are too strong to calibrate, and the values of R_c were derived by extrapolating the relation

$$\Delta \log R = \tfrac{2}{3} \Delta \log A ,$$

which holds good from $R = 15$ to $R = 40$.

TABLE X

ABSOLUTE CALIBRATION OF ROWLAND'S INTENSITY SCALE

El.	λ	R	$B \log A$	log NHf	log N_0	Res.	R_c
Na.......	5889	30	3.58	16.24	12.66	−0.10	25
	5896	20	3.35	15.94	12.59	−0.17	15
Al........	3961	20	4.28	16.67	12.39	−0.37	13
	3944	15	4.10	16.37	12.27	−0.49	9
Ca.......	4226	20	4.13	16.83	12.70	−0.06	18
Sr........	4607	1	0.54	14.34	13.80	+1.04	3
Sr^+.......	4077	8	3.39	16.15	12.76	0.00	8
	4215	5d?	2.65	15.85	13.19	+0.43	6
Ba^+......	4554	8	3.15	15.43	12.28	−0.48	6
	4934	3 and 4*	2.12	15.13	13.01	+0.25	5
Ca^+......	3933	1000	....	19.19	....	....	340
	3968	700	....	18.89	....	....	230
Mean.	....	....	....	....	12.76	....	....

* Given by Rowland as double; component intensities 3 and 4; see §10.

The average residual for one determination of log N_0 is ±0.35. The value previously found in another way[1] for the determination of log N from a single line was ±0.37.

The residuals show a systematic trend such as would be produced if the calibration of Rowland's scale gave differences in log N that are too great. A plot of the data suggests a reduction of the calibrated values by about 25 per cent; but so large a correction appears to be inconsistent with the much more extensive data ob-

[1] *Op. cit.*, p. 7.

tained from a study of the solar multiplets. Moreover, the residuals are already as small, on the average, as was to be anticipated. It may be that the calibration gives values too low for the numbers of atoms which produce the weaker lines; but the existing evidence is insufficient to determine what correction, if any, is required. The largest residual, for λ 4607, would be reduced to $+$o.50 if R were taken as 2 instead of 1, which would be in better agreement with Rowland's estimates for neighboring lines of equal strength; this would, however, give a smaller average residual than was to be expected. Taking the observations as they stand, we have log $N_o = 12.76 \pm$o.10, so that it requires 6×10^{12} "atoms" per square centimeter to produce a line of intensity o. The residuals show no definite evidence of a change of this quantity with the wave-length, although of course only a large change could be detected by so few observations, and the result may be adopted as generally applicable.

The mass of 6×10^{12} atoms of atomic weight m is 1.0×10^{-11} m grams. To produce a line of intensity o requires therefore o.1 m grams of matter per square kilometer of the sun's surface, or o.6 m millions of tons for the whole surface, 6×10^{12} km^2. The amount of an element which must exist in the sun's atmosphere to permit its spectroscopic detection is very great when measured by ordinary standards. For example, the platinum line at λ 3064.696 $(R = 1)$ indicates the existence of some five hundred million tons of the metal in the reversing layer. This is of course very small compared with the whole mass of the reversing layer, which, as we shall see later, probably exceeds 10^{15} tons.

10. *Numbers of atoms effective in different energy-levels.*—Accepting, then, for the present purpose, the calibration tables determined last year, we proceed to determine the "effective numbers" of atoms of the elements in their various energy-levels. The most direct way to do this is to calculate N by equation (1) for every solar line arising from the given level and add the results. This has two disadvantages: first, some lines are obscured in the sun by blends; second, on account of the approximately logarithmic character of Rowland's intensity scale, accidental errors of the estimates which make R too great increase the sum far more than errors in the opposite direction diminish it. When no theoretical information is available regarding

the relative intensities of the lines, as is the case for lines of a singlet system, or for inter-system combinations, these sources of error are unavoidable. Fortunately they affect the final sum in opposite directions. In normal multiplets, however, both may be avoided. If N' represents the sum of the number of atoms effective in producing the whole multiplet, and N that for a given line, one may write $N = N'F$, where F is a factor depending only on the quantum numbers. The values of these factors have been determined by several investigators.[1] Each line then gives an equation of the form

$$\log N' = B \log A - \log F \ . \tag{3}$$

By taking the mean of the values then found for all the lines of a given multiplet, the systematic effect of the errors of Rowland's estimates is eliminated, and the loss of some of the lines by blending is no longer serious. Errors may arise in multiplets when the actual intensities differ seriously from the theoretical. These will be serious only when some lines are abnormally faint. Such lines can almost always be recognized on the basis of laboratory intensities, and omitted from the mean.

One further complication sometimes arises. A good many of the stronger solar lines are given by Rowland as double, though all other evidence indicates that they are single. To add his intensities for the "components" gives much too high an intensity for the line, as is shown by comparison with other lines in the multiplet; but the assumption that the actual value of N is the sum of the values computed for the components as if they were separate lines gives results for N' in fair accordance with the others. As an example of the method, the strong multiplet $a^4F' - a^4G'$ of Ti II ($\lambda\,3349$, etc.) gives the results in Table XI.

No theoretical formulae for the relative intensities of different multiplets arising from the same lower level are yet available, except for a few very simple cases, and our best recourse is to add the individual values of N'. Their sum, which may be called M, expresses the whole number of atoms effectively at work for the given spectroscopic term. In a few cases, where the term separations are

[1] For numerical data see Russell, *Proceedings of the National Academy of Sciences*, **11**, 314, 1925.

very wide (as in *Tl* and *Pb*), the separate components have been treated independently, but this is rarely necessary.

In practice, it is usually found that much the greater part of M is contributed by a few multiplets, which correspond to transitions within the same family of terms (§2).[1] When these multiplets lie in the observable part of the solar spectrum, the values of M derived from the solar lines should be nearly correct. When, however, these strong groups are inaccessible, M will be too small. Present knowledge of spectra is sufficient to permit the recognition of these cases, except for a few complex spectra, notably the rare earths.

TABLE XI

Inner Quantum Number	R	$\log N$	$-\log F$	$\log N'$
5–6	7+2	3.8	0.48	4.3
4–5	8	3.9	0.59	4.5
3–4	5+5	3.5	0.72 .	4.2
2–3	3	2.0	0.84	2.8
5–5	3+3	2.4	1.64	4.0
4–4	5	3.1	1.52	4.6
3–3	3	2.0	1.64	3.6
4–3	2	1.3	3.20	4.5
3–2	2	1.3	3.10	4.4
Mean	. . . .	. . . .	. . . .	4.10

The results deduced in this way from the *Revision of Rowland's Table* are given in Table XII. The first two columns give the element and the spectroscopic term. The notation 4s, 3d, etc., has the significance described in §1. The designations of a few configurations which do not fit into this simplified scheme will be understood by those familiar with the subject. The third column gives the excitation potentials, measured from the lowest known energy-level, and the fourth, the number of lines, arising from the given term, which have been taken into account. For *Ti* and *Fe* all the lines of any strength were tabulated. For most of the rest, the lines which would obviously make but an insignificant contribution to the final sum were ignored, and the numbers are much smaller. The fifth column contains the value of $\log M$, obtained from Rowland's in-

[1] Many of these are listed in "Related Lines," *Mt. Wilson Contr.*, No. 341; *Astrophysical Journal*, **66**, 184, 1927.

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TABLE XII

Numbers of Effective Atoms

El.	Term		E	Lines	log M	log M Comp.
H.........	I	^2S	0.00	....	....	11.5
	2	$^2S, P$	10.15	I	3.5:	3.5
Li.........	2s	^2S	0.00	I	1.7*	1.7
Be.........	2s	^1S	0.00	....		1.8
	2p	^3P	2.72	2	>-2.0	0.1
Be$^+$........	2s	^2S	0.00	2	1.1	0.8
C..........	2p	$^3P'$	0.00	....		7.4
	3s	^3P	7.45	6	>0.9	1.1
	3s	^1P	7.59	I	$>>-1.$	0.6
N..........	2p	$^4S'$	0.00	....		7.6
	3s	$^4P'$	10.30	I	$>-0.7?$	-0.7
O..........	2p	^3P	0.00	....		9.0
	3s	^5S	9.11	3	1.3:	1.0
	3s	^3S	9.48	2	0.0:	0.5
Na........	3s	^2S	0.00	4	4.0	4.0
	3p	^2P	2.09	15	>2.7	2.7
Mg........	3s	^1S	0.00	I	$>>2.5$	7.0
	3p	^3P	2.70	11	4.8	5.3
	3p	^1P	4.33	10	>4.0	3.5
	4s	^3S	5.09	I	$>>0.8$	2.9
	$(3p)^2$	$^3P'$	7.14	I	>-0.7	1.6
Mg$^+$........	3s	^2S	0.00	....		7.7
	3d	^2D	8.83	2	0.3	0.9
Al..........	3p	^2P	0.00	5	4.6	4.6
	4s	^2S	3.13	2	$>>0.6$	1.4
Al$^+$........	3s	^1S	0.00	....		6.4
	3p	^1P	7.39	I	>-1.3	0.3
Si.........	3p	$^3P'$	0.00	....		7.0
	3p	^1D	0.77	....		6.0
	3p	^1S	1.90	2	3.9	4.4
	4s	^3P	4.91	10	$>>2.2$	2.8
	4s	^1P	5.06	I	$>>2.4$	2.2
Si$^+$........	3p	^2P	0.00	....		7.0
	$(3p)^2$	^2D	6.83	3	$>>0.9$	1.4
	4s	^2S	8.09	2	1.0	-0.4
S..........	3p	$^3P'$	0.00	....		5.7
	4s	$^5S'$	6.50	I	0.0:	0.0
K..........	4s	^2S	0.00	5	2.8:	2.8

* Lines appear only in sun-spots.

TABLE XII—*Continued*

El.	Term		E	Lines	log M	log M Comp.
Ca........	4s	¹S	0.00	3	4.1	4.5
	4p	³P	1.88	35	>3.6	3.6
	3d	³D	2.51	33	3.4	3.2
	3d	¹D	2.70	11	2.5	2.6
	4p	¹P	2.92	7	>2.8	2.2
Ca⁺........	4s	²S	0.00	2	6.7	6.7
	3d	²D	1.69	3	>4.1:	6.0
	4p	²P	3.12	5	3.5	4.5
	5p	²P	7.48	2	>>−0.7	0.8
Sc..........	4s	²D	0.00	15	1.6	1.9
	3d	⁴F′	1.43	12	>0.3	0.8
	3d	²F′	1.85	5	>−0.7	0.2
Sc⁺.........	4s	³D	0.01	15	3.7	3.5
	4s	¹D	0.31	3	3.0	2.8
	3d	³F′	0.61	11	>2.5	3.1
	3d	¹D	1.35	3	1.7	1.8
	3d	³P′	1.49	10	1.4	2.0
	(4s)²	¹S	1.45	1	>0.5	1.3
	3d	¹G	1.76	1	1.4	1.7
Ti..........	4s	³F′	0.02	37	3.6	3.5
	3d	⁵F′	0.82	28	3.0	2.7
	4s	¹D	0.90	6	2.0	2.1
	4s	³P′	1.05	26	>2.0	2.3
	3d	³F′	1.44	17	2.2	2.0
	4s	¹G	1.50	6	>1.4	1.8
	3d	⁵P′	1.73	17	1.9	1.6
	3d	³G	1.87	20	1.8	1.7
	4p	⁵G′	2.00	15	>1.3	1.8
	4p	⁵F	2.09	10	>1.3	1.7
	3d	³D	2.15	24	>1.1	1.2
	3d	³P′	2.23	5	>0.4	1.0
	3d	³H′	2.24	10	>1.5	1.5
	3d	¹G	2.26	6	>0.5	0.9
	4p	⁵D′	2.29	9	>0.6	1.4
	3d	³P′	2.32	7	>0.6	0.9
	3d	¹D	2.50	2	>−0.2	0.5
	3d	¹H′	2.57	6	>0.6	0.8
Ti⁺........	4s	⁴F′	0.02	22	4.5	4.8
	3d	⁴F′	0.13	19	>4.1	4.7
	4s	²F′	0.58	6	4.2	4.1
	4s	²D	1.08	16	3.0	3.5
	3d	²G	1.12	8	>3.2	3.7
	3d	⁴P′	1.16	16	3.2	3.5
	3d	²P′	1.22	8	3.2	3.1
	4s	⁴P′	1.23	13	3.3	3.4
	3d	²D	1.56	20	3.3	3.1
	3d	²H′	1.57	7	3.0	3.4
	4s	²G	1.88	9	3.2	3.1
	4s	²P′	2.04	9	2.4	2.4
	3d	²F′	2.58	4	>1.9	2.3

TABLE XII—*Continued*

El.	Term		E	Lines	$\log M$	$\log M$ Comp.
V	4s	$^4F'$	0.03	46	>2.3	3.5
	3d	^6D	0.28	49	2.9	3.0
	3d	^4D	1.05	29	>1.5	2.2
V^+	3d	^5D	0.00	....	....	4.8
	4s	$^5F'$	0.36	8	>3.9	4.6
	4s	$^3F'$	1.09	17	3.9	3.8
		$^3P'$	1.43	7	>1.8	3.1
		^3G	1.80	11	>2.3	3.3
		$^3H'$	2.50	15	>2.5	2.8
Cr.........	3d	^7S	0.00	8	4.3	4.0
	3d	^5S	0.94	8	>2.9	3.1
	4s	^5D	0.98	51	>3.6	4.1
	3d	^5G	2.53	46	2.4	2.7
Cr^+	3d	^6S	0.00	....	....	5.6
	4s	^6D	1.51	....	....	5.0
	4s	^4D	2.43	21	>3.4	4.0
		^2D	2.69	18	>>2.3	3.5
		^4D	3.09	9	>>2.7	3.5
Mn.........	4s	^6S	0.00	7	>3.6	5.1
	3d	^6D	2.14	41	3.6	3.7
	4p	^8P	2.29	14	3.5	3.4
	3d	^4D	2.91	26	>2.7	2.8
	4p	^6P	3.06	14	2.9	2.7
Mn^+........	4s	^7S	0.00	....	....	5.7
	4s	^5S	1.17	....	....	4.6
	3d	^5D	1.83	9	>>3.2	4.7
Fe.........	4s	^5D	0.07	86	>6.1	6.6
	3d	$^5F'$	0.99	133	5.7	5.7
	3d	$^3F'$	1.54	61	5.4	5.0
	3d	$^5P'$	2.19	86	4.3	4.3
	4s	$^3P'$	2.38	56	>3.4	4.2
	4p	$^7D'$	2.41	56	4.2	4.5
		$^3H'$	2.42	38	>3.7	4.5
		$^3F'$	2.57	36	>2.8	4.2
		^3G	2.71	38	4.1	4.1
	3d	$^3P'$	2.83	31	3.4	3.5
	4p	^7F	2.84	53	4.2	4.3
	4p	^7P	2.98	27	3.9	3.8
	4p	^3P	4.23	5	>2.4	2.4
Fe^+	4s	^6D	0.06	....	....	6.9
	3d	$^4F'$	0.33	....	....	6.7
	4s	^4D	1.04	11	>>4.0	5.9
	3d	$^4P'$	1.69	11	>>2.7	5.2
	4s	$^4P'$	2.68	12	>>2.6	4.3
	4s	$^4F'$	2.82	18	>>2.6	4.6
	$(4s)^2$	^6S	2.88	12	>>2.7	4.1
	4s	^4G	3.18	13	>>2.2	4.4
	4s	^4D	3.88	8	>>1.6	3.5

TABLE XII—*Continued*

El.	Term		E	Lines	log M	log M Comp.
Co..........	4s	$^4F'$	0.12	34	>3.6	5.0
	3d	$^4F'$	0.54	38	4.2	4.4
	3d	$^2F'$	0.98	15	3.9	3.7
Ni........	3d	^3D	0.12	25	5.1	5.1
	4s	$^3F'$	0.14	42	>4.4	5.5
	3d	^1D	0.42	17	4.5	4.3
	4s	^1D	1.67	14	2.8	3.6
	d^{10}	^1S	1.82	5	2.9	2.4
Cu........	3d	^2S	0.00	2	4.5	4.3
	4s	^2D	1.51	3	>>1.8	4.0
	(4p)	^2P	3.79	7	>1.1	1.5
	4p	^4P	4.82	1	>>−0.2	1.0
	4p	^4F	5.07	3	>>0.0	1.2
Zn........	4s	^1S	0.00	1	>>>0.7	4.9
	4p	^3P	4.02	7	1.9	2.1
	4p	^1P	5.77	2	0.5	0.2
Ga........	4p	^2P	0.00	1	>−0.1	0.2
Ge..........	4p	$^3P'$	0.05	....	....	2.5
	4p	^1D	0.88	3	1.4	1.5
	4p	^1S	2.02	2	0.1	−0.1
As........	4p	$^4S'$	0.00	....	....	0.6
	4p	$^2D'$	1.33	....	....	0.1
	4p	^2P	2.27	1?	>>−2.5?	−1.2
Rb........	5s	^2S	0.00	2	0.1:*	0.1
Sr..........	5s	^1S	0.00	1	0.6	0.6
	5p	^3P	1.80	4	>−0.4	−0.3
Sr$^+$........	5s	^2S	0.00	2	3.4	3.3
	5p	^2P	2.97	4	1.2	1.3
Yt..........	5s	^2D	0.03	9	0.8	0.8
	4d	$^4F'$	1.36	4	0.0	−0.2
Yt$^+$........	$(5s)^2$	^1S	0.00	3	1.4	1.6
	5s	^3D	0.10	18	2.5	2.4
	5s	^1D	0.40	4	1.6	1.7
	4d	$^3F'$	1.00	11	1.5	1.8
	4d	$^3P'$	1.71	6	0.1:	0.8
Zr..........	5s	$^3F'$	0.07	18	0.3	0.8
	4d	$^5F'$	0.66	9	0.0	0.3
Zr$^+$........	4s	$^4F'$	0.08	19	2.4	2.2
	3d	$^4F'$	0.34	12	>1.5	2.0
	4s	^2D	0.54	5	1.1	1.3
	4s	$^2F'$	0.75	7	1.8	1.3
	3d	$^2P'$	0.73	4	>1.1	1.0

TABLE XII—*Continued*

El.	Term		E	Lines	$\log M$	$\log M$ Comp.
Cb^+........	4d	^5D	0.00	....	....	0.8
	5s	$^5F'$	0.40	4	>0.3	0.6
Mo........	4d	^7S	0.00	....	....	0.3
	4d	^5S	1.33	1	−0.6	−0.9
	5s	^5D	1.35	5	>−1.2	0.0
Mo^+........	4d	^6S	0.00	....	....	1.3
	5s	^6D	1.5?	....	....	0.7?
	5s	^4D	2.4?	2	>−1.7	−0.2?
Ru........	4d	$^5F'$	0.16	5	>0.0	0.9
	4d	$^3F'$	0.97	3	0.0	0.0
Rh........	4d	$^4F'$	0.27	8	−0.6	−0.3
	4d	$^2F'$	0.88	1	>−0.9	−1.1
Pd........	d^{10}	^1S	0.00	....	....	0.1
	4d	^3D	1.00	5	0.4	0.4
	4d	^1D	1.45	2	>−0.6	−0.4
Ag........	4d	^2S	0.00	2	0.0	0.0
Cd........	5s	^1S	0.00	1	>>−0.7	2.1
In........	5p	^2P	0.00	1	−0.4*	−0.1
Sn........	5p	$^3P'$	0.21	....	....	0.3
	5p	^1D	1.06	2?	−1.0?	−0.7
Sb........	5p	$^4S'$	0.00	....	....	0.3
	5p	$^2D'$	1.14	....	....	−0.3
	5p	^2P	2.15	2	>−2.0	−1.3
Ba^+........	6s	^2S	0.00	2	3.0	2.9
	5d	^2D	0.65	3	>2.7	3.0
	6p	^2P	2.60	4	1.2	1.2
La^+........	5d	$^3F'$	0.12	12	1.4	1.5
		^1D	0.17	9	0.9	0.9
	6s	^3D	0.32	13	1.3	1.2
		^1S	0.91	1	>−0.5	−0.5
	5d	^1G	0.92	1	0.0	0.5
Ce^+........	....		0.4:	249	2.1	2.1
Pr^+........	....		0.4:	18	0.3:	0.3
Nd^+........	....		0.4?	107	1.6	1.6
Sa^+........	....		0.4?	67	1.1	1.1
Eu^+........	....		0.4:	5	1.0:	1.0
Gd^+........	....		0.5:	15	0.7:	0.7:

TABLE XII—*Continued*

El.	Term		E	Lines	log M	log M Comp.
Dy^+........	....		0.5:	12	1.2:	1.2
Er^+........	....		0.5:	2	−0.3:	−0.3
Hf^+........	....		0.7	28	−0.1	−0.1
W..........	6s	^{5}D	0.44	5	>−0.6	−0.6
Ir..........		^{2}D	0.18	1?	−1.5?	−0.5
Pt..........		^{3}D...	0.04	3	1.0	1.5
Tl..........	6p	^{2}P$_1$	0.00	1?	−0.9:?	−0.9
		^{2}P$_2$	0.96	1?	−1.5:?	−1.4
Pb........	6p	^{3}P$_0'$	0.00	....		0.0
		^{3}P$_1'$	0.97	1	>−1.7	−0.3
		^{3}P$_2'$	1.32	1	−0.7	−0.4
		^{1}D$_2$	2.65	1	>−1.3	−1.6
CN........	....		o ?	872	3.2	....
C_2.........	....		o ?	422	1.3	....
CH........	....		o ?	155	3.0	....
NH........	....		o ?	157	2.1	....
OH........	....		o ?	185	3.0	....
BO........	....		o ?	28	1.4*	....

tensities as described above, and represents the "absorbing power" of the term. For the H and K lines Unsöld's measures (§ 9) are used.

The sign $>$ preceding an entry signifies that important multiplets arising from the term are known to be out of reach in the infrared or ultra-violet, and $>>$ that such multiplets are much stronger than those observed. Lines which appear only in sun-spots are denoted by an asterisk. A colon means, as usual, that the results are uncertain, and a question mark, that the attribution to the given element is doubtful. For C, N, O, S, K, and Rb, most or all of the lines are in the deep red, beyond the limit of Rowland's original work, where the scale of intensities may differ considerably from Rowland's and has not been independently calibrated. These values of log M may be too low. For hydrogen, the situation is peculiar.

We should expect the widths and intensities of $H\beta, H\gamma, H\delta$ to diminish rapidly, since the transition probabilities fall off. Unsöld's measures,[1] however, show that this is not the case, and some exceptional influence must be at work—perhaps the Stark effect. The $H\alpha$ line must also be affected, though to a less degree. The tabular value is derived from Rowland's intensity for this line alone, without correction for the factor 0.64, which expresses the theoretical value for $H\alpha$ relative to the sum of the whole Balmer series. It may nevertheless be too great. Unsöld's measures of the width of this line, treated similarly, give log $M = 4.1$. This is probably considerably too great, for the reasons stated. For the rare earths, whose spectra have not been analyzed, the sum of the values of N for all the unblended lines has been taken, and increased pro rata in proportion to the number of blended lines recorded. The values of the average excitation potential for these elements are rough estimates based on the data for La^+ and Hf^+. Many of the lines of the latter are unclassified, and the same method has been applied to them.

The band spectra due to compounds, which appear at the end of the table, have been treated in the same way. These bands are all absorbed by unexcited molecules, but, owing to the vibrational and rotational energy, the excitation potentials may be somewhat above the zero values entered in the table. The fifth column of the table contains values of log M calculated in the way described below (§13). These values have been included, for completeness, in a number of cases where no observations can be made.

11. *Discussion of these data.*—Much has been written on the theoretical distribution of the energy states of the atoms in a stellar atmosphere. An exact discussion would be very complicated, but, fortunately, there is good reason to believe that the most simple and obvious approximations should give results close to the truth.

The temperature of the reversing layer doubtless increases toward its base, but it is probable that the change is relatively small. According to Eddington,[2] it increases from 0.81 to 0.88 times the effective temperature T_e between the outer boundary and the depth corresponding to the optical thickness $\tau = 0.25$. These values hold

[1] *Zeitschrift für Physik*, **46**, 778, 1928.

[2] *The Internal Constitution of the Stars*, pp. 332 and 335.

for the integrated light. For the center of the disk the range is from the same lower limit to $0.91\ T_e$. Since most of the material is in the deeper layers, the assumption $T = 0.87\ T_e$ would appear to be reasonable. For the sun, $T_e = 5730°$ and $T = 4980°$.

The pressures in the upper and lower parts of the reversing layer must differ very greatly. Milne[1] has just shown, however, that the assumption of a uniform pressure gives surprisingly good results. Although the opacity actually increases gradually with the depth, the line contours should be very similar to those produced by an atmosphere devoid of general opacity and overlying a solid photosphere, provided that the amount of matter in this fictitious atmosphere were equal to that which is actually above the optical depth $\tau = 1/3$. The "number of atoms above the photosphere" then takes on a definite meaning. He shows also that the total numbers of neutral and ionized atoms above any depth will be very nearly the same as those calculated from the elementary formula of Saha, with an electronic pressure one-half of the value at the given depth. The effects of a chromosphere supported by radiation pressure are excluded from consideration.

In what follows, we shall therefore consider the sun's atmosphere as having a definite temperature T, and a definite electronic pressure P. In thermodynamic equilibrium, the number M_0 of neutral atoms in any energy state is then given by the equation

$$\log M_0 = \log A_0 + \log W - \frac{5040\ E}{T}, \qquad (4)$$

where A_0 is a constant depending on the abundance of the element considered, W is the total quantum weight of the state or the corresponding spectroscopic term, and E the excitation potential in volts. The value of W is the product of the multiplicity of the term (1, 2, 3, for singlets, doublets, triplets) by 1, 3, 5, 7, for S, P, D, F terms. For terms arising from electron configurations involving two equivalent s electrons, these values should be doubled.[2] Such terms occur in Be, Mg, Ca to Zn, Sr to Cd, and Ba to W for the terms de-

[1] *Monthly Notices, R.A.S.*, **89**, 3 and 17, 1928.

[2] W. Heisenberg, *Zeitschrift für Physik*, **38**, 411, 1926. For the application to more complex spectra, the writer is indebted to a conversation with Professor Sommerfeld.

noted by 2s, 3s, etc., in Table XII. A few similar cases in ionized atoms are denoted by $(4s)^2$ and the like. For an energy state of an ionized atom we have

$$\log M_1 = \log A_1 + \log W_1 - \frac{5040E}{T} , \qquad (5)$$

where A_1 is the abundance factor for ionized atoms. This is connected with A_0 by Saha's equation

$$\log A_1 - \log A_0 = -\frac{5040I}{T} + \tfrac{5}{2} \log T - 6.5 - \log P . \qquad (6)$$

If we set

$$\tfrac{5}{2} \log T - 6.5 - \log P = \frac{5040I_0}{T} , \qquad (7)$$

this means

$$\log A_1 = \log A_0 + \frac{5040}{T} (I_0 - I) . \qquad (8)$$

The constant I_0 is the ionization potential of an element which would be just half ionized under the conditions. It may be taken as defining the "level of ionization" in the star's atmosphere.

We have finally to take into consideration the fact that the atmosphere may not be in thermodynamic equilibrium. The comparison of solar and stellar spectra affords evidence that this is the case.[1] The lines arising from excited states are stronger in the cooler stars than the elementary theory expressed by equation (4) predicts. The degree of ionization appears to be unaffected. We may take account of this by writing

$$\log M = \log A_0 + \log W - \frac{5040}{T} (E - C) , \qquad (9)$$

and similarly for ionized atoms. It is assumed that C is a function of E, which must be determined empirically. The evidence from the stars indicates that C is small at first, but increases rapidly when E exceeds 2 or 3 volts. Were it not for the limitation of the solar record, the determination of this correction would be simple, especially since for the sun's atmosphere $5040/T = 1$ within the un-

[1] Adams and Russell, *Mt. Wilson Contr.*, No. 359; *Astrophysical Journal*, **68**, 11, 1928.

certainty of estimation. Each value of $\log M$ in Table XII leads by (9) to one of $\log A - C$ for the same element, and a plot of these for elements such as Fe and Ti would give values of C up to $E = 4.5$. But so many of the lines arising from these higher levels are in the infra-red that this is impracticable.[1] The data are, however, sufficient to show that C is small if E is less than 2 volts, and to give reliable values of $\log A_0$ for the neutral atoms of many elements, and of $\log A_1$ for a smaller number of ionized atoms. When we know A_0 and A_1 for the same element, we can find I_0 by (8). The determinations of this quantity from different elements are in good agreement (see below). Taking the mean, we can then find A_1 for any element, if we know A_0 and I.

Now there are a few solar lines of Si^+, Mg^+, and Al^+, for which E is between 7 and 9 volts. Having found A_1 for these elements, as just described, we may use these lines to obtain the values of C corresponding to these large values of E. The results are discordant. The Si^+ lines $\lambda\lambda$ 6347, 6371 give $C = 2.6$ for $E = 8.09$; Mg^+ λ 4481, $C = 0.7$, $E = 8.83$; and Al^+ λ 3900, $C = -0.5$, $E = 7.39$. In all these cases the lines are the strongest which arise from atoms in the given state, and the correction on this account is small.

The Al^+ line is very faint and deserves half weight. We therefore adopt as a mean $C = +1.2$ for $E = 8.2$ volts. In default of further information, we will assume that $C = 0.15E$ for all values of E.

A more satisfactory determination of the important correction is much to be desired; but no further solar data are available. In a star of earlier spectral type, such as Procyon, a larger number of enhanced lines would be available, and determinations of the correction, made for dwarf stars, might perhaps be extended to apply to the sun. To use giant stars for this purpose would be unsafe.

As matters stand, the determination of the solar abundance factors A_0 and A_1 is little influenced by this uncertainty for the metals, while the values for the non-metals, especially those of low atomic weight, remain considerably uncertain.

12. *Level of ionization in the sun.*—There are five elements for which the principal lines of both the neutral and ionized atoms are

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[1] This difficulty does not affect the comparison of the intensity of the same lines in the sun and a star, on which last year's results were based.

accessible. Each of them may be used to determine the level of ionization I_0 by the equation

$$I_0 = I + \frac{T}{5040} (\log A_1 - \log A_0) . \tag{10}$$

The results are shown in Table XIII. The five values agree remarkably well, when we consider that they have been determined in some cases (Ca) from extremely strong lines, and in others (Sc, Yt) from very weak ones. Giving double weight to the values for Ca and Ti, we find the mean value $I_0 = 8.26 \pm 0.08$ volts. This probable error, which is derived from the residuals, should be taken only as an indication of the consistency of the determinations. The value $I_0 = 8.3$ volts will be adopted in the present discussion.

TABLE XIII

IONIZATION IN THE SUN

	ELEMENT				
	Ca	Sc	Ti	Sr	Yt
log A_0............	4.2	0.3	2.1	0.3	−0.4
log A_1............	6.4	2.5	3.3	3.0	1.2
log A_1−log A_0.....	2.2	2.2	1.2	2.7	1.6
I................	6.1	6.6	6.8	5.6	6.5
I_0................	8.3	8.8	8.0	8.3	8.1

By equation (7) this corresponds to the electron pressure $P = 3.1 \times 10^{-6}$ atm. $= 3.1$ dynes/cm². These values of I_0 and P depend on the assumed temperature of the solar atmosphere. If, for example, we had taken $T = 5740°$, as Milne does in his latest paper,[1] we would have found $I_0 = 8.53$ volts and $P = 2.5 \times 10^{-5}$ atm. The computed pressure is much more sensitive to changes in the assumed temperature than is the value of I_0. The latter appears, therefore, to have considerable advantage for the specification of the state of a stellar atmosphere. If only the farther ultra-violet were accessible, the enhanced lines of the more difficultly ionizable elements could be observed, and the value of I_0 found almost as a direct result of observation, independent of any theory except that involved in the calibration of the lines. The pressure here derived is in fair agreement with

[1] *Monthly Notices, R.A.S.*, **89**, 35, 1928.

the values found by the same method from the calcium lines in stars by Miss Payne and Mr. Hogg[1] ($P = 2.54 \times 10^{-6}$ atm. in class Go) and by Unsöld[2] from the strontium lines (3.3×10^{-6}). From the calcium lines Unsöld finds 3.4×10^{-7}. The difference arises mainly from the fact that the other calcium lines used in the present work give a greater value for A_0 than does λ 4226. Unsöld's value, which rests on precise measurements, is doubtless more accurate, but the mean value resulting from the calibration of Rowland should clearly be used in the present work.

13. *Abundance of the elements in the sun's atmosphere.*—With the constants thus determined, we may now compute the number, M, of atoms which are in any given energy state, neutral or ionized, by the equations

$$
\left.
\begin{aligned}
\log M &= \log A_0 + \log W - 0.85E \text{ (neutral atom)}, \\
\log M &= \log A_1 + \log W - 0.85E \text{ (ionized atom)}, \\
\log A_1 &= \log A_0 + I_0 - I.
\end{aligned}
\right\}
\tag{11}
$$

Each observational value of $\log M$ gives one of $\log A_0$ or $\log A_1$. Mean values of these for each element are given in Table XIV and the values of $\log M$ calculated from these in Table XII, under the heading "Log M Comp." In adopting these values and adjusting those of A_0 and A_1 to satisfy the ionization equation, the accuracy of the individual values of $\log M$ has been kept in mind. Examination of Table XII shows that, for the more abundant metals, a change in $\log A_0$ and $\log A_1$, by 0.1 or 0.2 at most, is all that is permissible. For some elements, such as *Si*, the data are discordant, and the uncertainty greater. There are many elements, however, for which the determination rests only on a few faint lines, and in these cases the tabular values are only an indication of the order of magnitude of the results. Such cases are denoted in the table by a colon, while a question mark indicates that the origin of the lines is doubtful. The remaining columns of Table XIV give quantities related to the abundance of the atoms in the solar atmosphere. S_0 is the whole number of neutral atoms per unit area, derived from the sum of the values of M for the different energy levels, and S_1, the

[1] *Harvard Circular*, No. 334, 1928.

[2] *Zeitschrift für Physik*, 46, 778, 1928.

TABLE XIV

Abundance of Elements and Compounds in the Sun

El.	log A_0	log A_1	log S_0	log S_1	log T	log Q
H	11.2::	5.7::	11.5::	5.7::	11.5::	11.5::
x Li	− 1.2:	1.7:	− 0.9:	2.0:	2.0:	2.8:
Be	1.5	0.5	1.8	0.8	1.8	2.8
o C	6.5:	3.6:	7.4:	4.4:	7.4:	8.5:
N	7.0?	0.8?	7.6?	1.8?	7.6?	8.7?
O	8.0:	2.7:	9.0:	3.3:	9.0:	10.2:
x Na	3.7	6.9	4.0	7.2	7.2	8.6
x Mg	6.7	7.4	7.0	7.7	7.8	9.2
x Al	3.8	6.1	4.6	6.4	6.4	7.8
x Si	6.0	6.2	7.0	7.0	7.3	8.8
S	4.8:	2.8:	5.7:	3.4:	5.7:	7.2:
x K	2.5:	6.5:	2.8:	6.8:	6.8:	8.4:
x Ca	4.2	6.4	4.6	6.7	6.7	8.3
o Sc	0.6	2.3	1.9	3.6	3.6	5.3
x Ti	1.9	3.4	3.6	5.2	5.2	6.9
x V	1.8	3.4	1.9	5.0	5.0	6.7
o Cr	3.2	4.8	4.4	5.7	5.7	7.4
o Mn	4.0	4.9	5.1	5.8	5.9	7.6
x Fe	5.0	5.5	6.7	7.1	7.2	9.0
o Co	3.4	3.9	5.1	5.4	5.6	7.4
o Ni	4.0	4.7	5.7	5.7	6.0	7.8
x Cu	4.0	4.6	4.3	4.9	5.0	6.8
x Zn	4.6	3.5	4.9	3.8	4.9	6.7
o Ga	− 0.6:	1.7:	0.2:	2.0:	2.0:	3.8:
o Ge	1.6	2.0	2.5	2.8	3.0	4.9
As	0.0?	− 1.3?	0.6?	− 0.7?	0.6?	2.5?
o Rb	− 2.8:	1.4:	− 2.5:	1.7:	1.7:	3.6:
x Sr	0.3	3.0	0.6	3.3	3.3	5.2
Yt	− 0.5	1.3	0.8	2.6	2.6	4.5
o Zr	− 0.7	0.8	0.9	2.5	2.5	4.5
Cb	− 1.8:	− 0.6:	− 0.2:	1.0:	1.0:	3.0:
o Mo	− 0.5	0.5	0.5	1.4	1.4	3.4
o Ru	− 0.5	0.1	1.0	1.6	1.7	3.7
Rh	− 1.5	− 0.9	− 0.3	0.5	0.5	2.5
Pd	0.1	0.1	0.6	0.9	1.1	3.1
Ag	− 0.3	0.7	0.0	1.0	1.0	3.0
Cd	1.8:	1.3:	2.1:	1.6:	2.2:	4.2:
o In	− 2.8:	− 0.3:	− 2.0:	0.0:	0.0:	2.1:
Sn	− 0.5?	0.4?	0.3?	1.2?	1.2?	3.3?
Sb	− 0.3:	− 0.3	0.4:	0.7:	0.8:	2.9:
o Ba	− 0.5	2.6	− 0.2	3.3	3.3	5.4
o La	− 2. :	0.3	− 0.7:	1.8	1.8	3.9
Ce				2.4	2.4	4.6
Pr				0.6:	0.6:	2.8:
Nd				2.0	2.0	4.2

TABLE XIV—*Continued*

El.	log A_0	log A_1	log S_0	log S_1	log T	log Q
Sa				1.5	1.5	3.7
Eu				1.4:	1.4:	3.6:
Gd				1.1:	1.1:	3.3:
Dy				1.6:	1.6:	3.8:
Er				0.1:	0.1:	2.3:
Hf				0.4	0.4	2.6
W	− 1.5	− 1.5	− 0.1	− 0.1	0.2	2.5
Ir	− 1.5?	− 1.5?	− 0.5?	− 0.5?	− 0.2?	2.1?
Pt	0.4	0.0	1.5	1.0	1.6	3.9
Tl	− 1.2?	1.1?	− 0.8?	1.4?	1.4?	3.7?
Pb	0.0	0.9	0.2	1.2	1.2	3.5
CN			3.2		3.2	4.6
C_2			1.3		1.3	2.7
CH			3.0		3.0	4.1
NH			2.1		2.1	3.3
OH			3.0		3.0	4.2
BO			1.4		1.4	2.8

number of ionized atoms. In a few cases such as *Ru* II and *Rh* II, the calculation of S_1 involves assumptions regarding the nature of the lowest terms in spectra which have not yet been analyzed; but the uncertainty thus arising is much less than that of the observational data for these elements. The next column gives log T, where T is the total number of atoms of the element considered in both stages of ionization. Doubly ionized atoms may safely be neglected. They should be relatively most numerous for *Ba*, for which log $S_2 = 1.3$, but this is only 1 per cent of the number of singly ionized atoms. For the rare earths the values of S_1 have been directly calculated by the approximate process described in §10. The ionization potentials are unknown, and S_0 cannot be given; there is no doubt, however, that it is small, and that no serious error is committed by neglecting it, as has been done here. For the band spectra, S_0 gives the number of neutral molecules. Finally, Q represents the total mass of the atoms or molecules of the substance per unit area of the sun's surface. The tabular values are obtained by multiplying T by the atomic or molecular weight. We have already found that the unit of T represents 6×10^{12} atoms per square centimeter. That of Q corresponds, therefore, to 1.0×10^{-11} g/cm².

In a number of cases special considerations have been applied

in deriving A_0 or A_1 from the observations. For several elements, many or most of the lines arising from the best observable level are out of reach in the ultra-violet, and the observed value of log M must be corrected from the probable intensity. The corrections which have been applied are $+1.3$ for As, $+0.3$ for Cb^+, $+0.7$ for Sb, $+0.5$ for W and Pt, and $+1.0$ for Ir. Though rough estimates, they probably improve the tabular values. For Cd, only a single inter-system combination, $^1S_0 - {}^3P_1$, is observed (λ 3261). For this line Prokofjev[1] has found that the number of effective resonators is $1/600$ that for the resonance line $^1S - {}^1P$. The values of the corresponding ratios for lines of Ca and Zn, derived from the solar data, agree with his formula as well as could be expected. The correction $+2.8$ for the Cd line may therefore be adopted. For Mo^+ the analysis of the spectrum is fragmentary, and the relative energy-levels of the terms have been assumed to be the same as in Cr^+, a permissible assumption, as very rough values will suffice.

Finally, there are three elements, Li, In, and Rb, whose lines appear only in sun-spots. To attempt to correct for the change of ionization theoretically would lead us too far. It may suffice to take the observed intensities of a number of faint lines of other metals of easy ionization in the same part of the spectrum and thus find ratios of the change in log N from the spot to the disk. Thirty-seven lines between λ 4350 and λ 4650 give a mean change of -1.9, which has been adopted for In λ 4511; thirty between λ 6100 and λ 6600 give $+2.6$, which has been adopted for Li λ 6708, and in default of other data, for Rb $\lambda\lambda$ 7947, 7800.

Table XIV contains the principal conclusions of the present paper. The main source of uncertainty which affects them is the magnitude of the correction for departure from thermodynamic equilibrium. For the metals, this is always small, and the tabular data may be accepted with confidence. For the non-metals it is much greater (except for Si). For C, N, O, and S, the value of E averages 8.4 volts, while for H it is 10.2. The uncertainty of the correction C is at least 10 per cent of these values. To increase this correction would diminish the very large values for the abundance of these elements. For hydrogen the uncertainty is increased, since

[1] *Ibid.*, **50**, 708, 1928.

it is unknown how much of the width of the lines, which was clearly the main criterion in Rowland's estimates of intensity, arises from special causes. Anything short of an extreme correction for both these factors would still leave hydrogen the most abundant element by weight, and more abundant, by number of atoms, than all the rest together. Even with a liberal correction, oxygen and its neighbors remain among the most abundant elements by weight, and still more by number.

The values of log Q are plotted in Figure 3—the more reliable ones by solid dots and the less trustworthy by open circles. Two features of the distribution are conspicuous. First is the general downward trend toward the right, corresponding to a diminution in the abundance with increasing atomic number. The fact is familiar; its interpretation, less certain. The faintness of the lines of the heavy elements in the sun is commonly attributed to the tendency of the heavy atom to diffuse downward, below the photosphere. If this were the main explanation we should expect the heavy elements following *Ba* to be considerably less abundant than those which succeed *Sr;* but the figure shows that this is not the case and suggests a relatively rapid fall for the lighter elements from *H* about as far as *Zr* and a very slow decrease for the heavier ones.

Stirring of the solar atmosphere by currents and other forms of turbulence favors a uniform mixture. This process occurs on an enormous scale in sun-spots, where the material must ascend from a considerable depth.[1] The fact that the lines of La^+ and other heavy elements, which are completely ionized even in the spots, are not perceptibly strengthened in the spot spectrum indicates that the difference in composition is small at the depth from which the ascending vortex comes. It does not appear necessary, therefore, to assume that downward diffusion depletes the sun's atmosphere of the heavier elements, though the possibility of such an influence remains.

Second, there is a conspicuous zigzag arrangement of the points, which represents the well-known fact that the elements of even atomic number are more abundant than those whose numbers are odd. The generality of this rule is well illustrated by the diagram. Every

[1] Russell, *Astrophysical Journal*, **54**, 293, 1921.
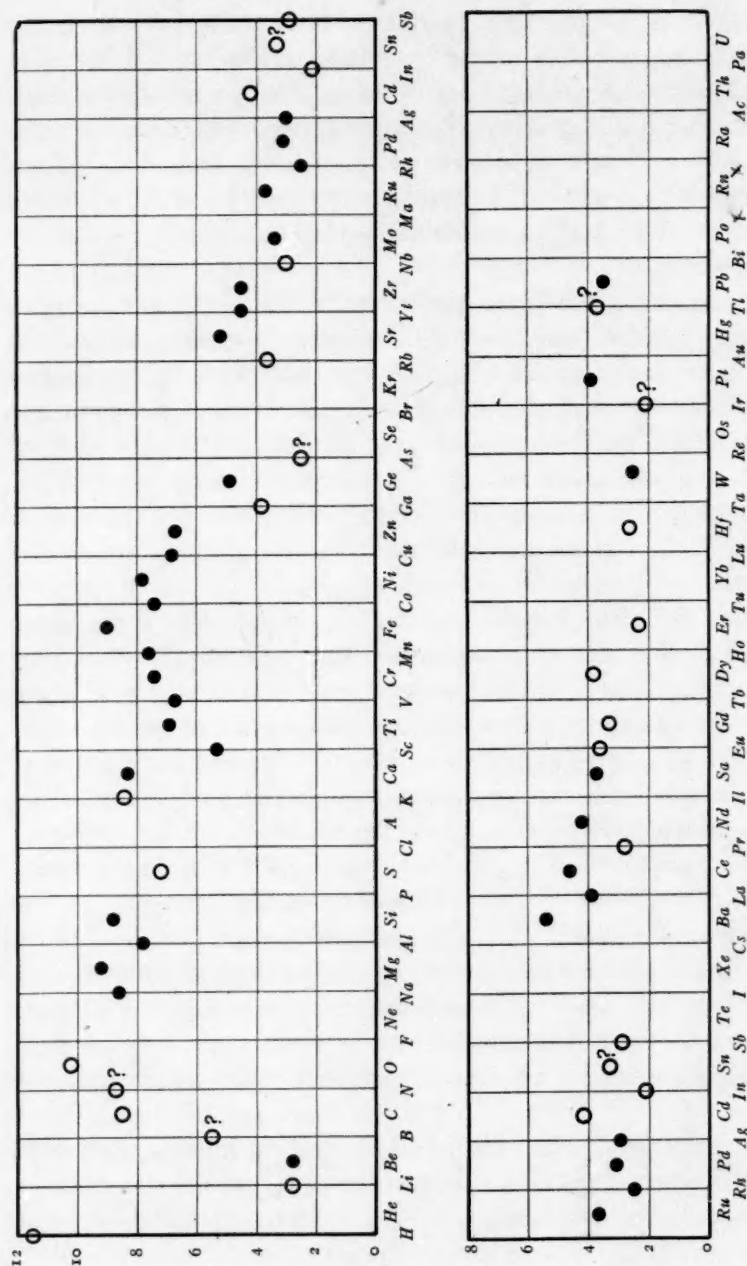
FIG. 3.—Values of log Q, where Q represents the total mass of the atoms or molecules of an element per unit area of the sun's surface.

element of even number except *Be* is more abundant than the mean of the adjacent elements, when both these are known, and every odd element less abundant, with the exception of *Eu*, for which the data are uncertain. For *Tl*, which also looks like an exception, they are still more doubtful. There is little doubt, however, that *Na* and *K* are real exceptions, for if *Ne* and *A*, which precede them, were anything like as abundant, we might expect them to show in the flash spectrum. The average difference between $\log Q$ for an even element and the mean for the two adjacent odd ones is $+1.03$ (14 cases), while for an odd element and the adjacent even ones it is -1.05 (15 cases). If the weaker determinations are excluded, these values become $+0.86$ for six even elements and -0.93 for ten odd ones. This indicates that the even elements are, on the average, about ten times as abundant as the odd. Among the rare earths and the heavier elements, only those with even atomic numbers have been conclusively identified in the sun. Certain elements stand out as rare in comparison with their neighbors—notably *Sc*, *Ga*, and *In*. These are well-known chemical rarities; it is surprising, however, to find *As* behaving in the same way. It may be that the estimated correction, which allows for the fact that all but weak lines of this element are inaccessible, was too small. The most striking examples of all are *Be* and *Li*. The latter is not ordinarily considered a rare element, but it is evidently present only in small proportions in the sun. The most abundant elements, compared with the mean of their neighbors, are *Fe* (and probably *Na* and *K*). If these individual differences are corrected for the general tenfold difference between odd and even elements, what remains is surprisingly small. *Sc* and *Ga* are one-twentieth and one-tenth as abundant as might be expected on this basis, and *Fe* only three times more abundant.

The abundance of an element is probably a function of yet unknown properties of the structure of the atomic nucleus. The results here obtained suggest that, in general, these properties change slowly and rather regularly with the nuclear charge. The very low abundance for *Li* and *Be* suggests that nuclei containing so few component parts may be hard to keep together. The amounts of the compounds which are present in the sun's atmosphere are surprisingly small. No one would have guessed, for example, that *CN*

was but one-fifth as abundant as Sc. A moment's consideration, however, shows that molecules have a great advantage in the banded nature of their spectra. A single electron transition, which in an atom gives rise to at best but a very few multiplets, will, in a molecule, produce a whole system of bands, containing perhaps thousands of lines. The width of a line and the amount of light which it cuts out of the spectrum vary approximately as the square root of the number of atoms which are acting. To break up one strong line into a hundred faint ones increases tenfold the total effect on the spectrum—as much as a hundred fold increase in the number of atoms would do, if the original lines were unaltered.

For any atom which enters into one of these compounds, there are great numbers of the same kind in the free state. The values of $\log S$ for the combined atoms are, in fact, found to be 4.5 for C, 4.4 for N, 4.2 for O, and 3.3 for H. Those given in Table XIV for the free atoms exceed these by 2.9, 3.3, 4.8, and 8.2, respectively. On the face of the record, then, only one atom in a thousand, at most, enters into combination. This accords with the fact that the band spectra are at the point of disappearance in class Go. From the BO bands, which appear only in the spots, the amount of combined boron corresponds to $\log S = 2.4$. For the free atoms it is probable that $\log S = 5.5$ or perhaps more. This value has been plotted with a question mark in Figure 3. There is but one element known to exist in the sun for which no estimate of abundance has now been made—and this is He. The intensity of its lines in the chromosphere shows that it must be present in considerable amount, but no quantitative estimate seems possible.

The total quantity of the metallic elements (among which Si should be included for astrophysical purposes) in the solar atmosphere can be determined with considerable confidence from the spectrum. That of the non-metals is much less certain. It is fortunate, however, that the metals provide almost all of the ions and electrons. The values of S_1 in Table XIV indicate that the non-metals provide only 1/200 of the free electrons. If the correction for departure from thermodynamic equilibrium should be wholly disregarded, the calculated abundance of hydrogen—already very great —would be increased thirty fold; but even then the non-metals

would provide only 13 per cent of the electrons. The table should therefore give a practically complete census of the charged particles in the atmosphere. Summing the values of S_i, we find, for the whole number of ions or electrons, 1.05×10^8 of our arbitrary units, or actually 6.3×10^{20} per square centimeter of the sun's surface. Six elements, Na, Mg, Si, K, Ca, and Fe, contribute 95 per cent of these. Mg alone accounts for nearly half the total; Ca for 5 per cent. The number of neutral atoms of the metals comes out 2.6×10^7 units, or 1.6×10^{20} atoms/cm². Mg, Si, and Fe contribute 96 per cent of the total. The whole number of metallic atoms in the solar atmosphere may therefore be taken as 8×10^{20} per square centimeter, of which 20 per cent are neutral and 80 per cent ionized.

The total mass of the metals is found to be 4.2×10^9 in our units, or 42 mg/cm². The mean atomic weight is 32. The six most abundant elements account for 94 per cent of the whole mass. The amounts of these elements in the solar atmosphere, as determined in the present work, are given for reference in Table XV. Those of the compounds are added at the bottom. This table brings out very clearly the extraordinary preponderance of the metals in the second short and the first long period. The only rare metal among these, Sc, is more abundant than any one of the heavier metals except Ba. For all these metals together the total mass is only 0.7 unit—much less than that of any metal in the favored region, except Sc. The "heavy metals," from Ba onward, appear to be somewhat less abundant than those from Ge to Sb, but this difference is relatively small. The extreme rarity of Li and Be is conspicuous. The correction factors for the non-metallic elements are too uncertain to justify their inclusion in the table. With the data as they stand, the number of atoms of C, N, and S together is 7.5×10^7 of our units— about half that for all the metals; that of oxygen is 10^9, and of hydrogen 3×10^{11}. By weight the abundances are 10^9 for C, N, and S; 1.6×10^{10} for O; and 3×10^{11} for H. It appears to be a safe conclusion that C, N, and S are not more abundant, either by number or by weight, than the commoner metals. The conclusion from the "face of the returns" is that O is four times, and H eighty times, as abundant by weight as all the metals together. These numerical values should not be stressed; but the great abundance of H can

hardly be doubted. It is, however, very difficult to estimate it from the intensity of the Balmer lines. The great width of these may be partly due to Stark effect caused by the fields of neighboring ions or electrons.[1] This would make the lines stronger as well as wider; for the separate components into which the line is divided, if acting independently, would produce a greater total "absorption" than a single line. This should still happen even though the fields differ from atom to atom, so that the components are smeared into

TABLE XV

AMOUNTS OF THE METALS IN THE SOLAR ATMOSPHERE, BY WEIGHT

(Unit 100 mg per Square Meter)

Li	0.0006	Zn	5.	Sb	.001:
Be	0.0006	Ga	0.006:	Ba	.25
Na	400.	Ge	.08	La	.008
Mg	1500.	As	.0003?	Ce	.04
Al	60.	Rb	.004:	Pr	.001:
Si	600.	Sr	.15	Nd	.015
K	250.:	Yt	.03	Sa	.005
Ca	200.	Zr	.03	Eu	.004:
Sc	0.2	Cb	.001:	Gd	.002:
Ti	8.	Mo	.003	Dy	.006:
V	5.	Ru	.005	Er	.0002:
Cr	25.	Rh	.0003	Hf	.0004
Mn	40.	Pd	.0012	W	.0003
Fe	1000.	Ag	.001	Ir	.0001:
Co	25.	Cd	.015:	Pt	.008
Ni	60.	In	.0001:	Tl	.005?
Cu	6.	Sn	0.002?	Pb	0.003
CN	0.04	CH	0.012	OH	0.015
C₂	0.0005	NH	0.002	BO	0.0006

a diffuse line.[2] The tabular value, which is one-fifth of that calculated by Unsöld from the width of $H\alpha$, is already partially corrected.

14. *Comparison with the results of other investigations.*—The most important previous determination of the abundance of the elements by astrophysical means is that by Miss Payne,[3] who determined, by Milne's method of marginal appearances, the relative abundance of

[1] Russell and Stewart, *Astrophysical Journal*, **59**, 197, 1924; Eddington, *Internal Constitution of the Stars*, p. 354, 1926.

[2] It may be noticed, in passing, that the effect should contribute toward the strengthening, in sun-spots, of lines which have complicated Zeeman patterns.

[3] *Stellar Atmospheres* ("Harvard Observatory Monographs," No. 1), Cambridge, Mass., p. 184, 1925; also *Harvard Observatory Bulletin*, No. 835, 1926.

eighteen of the most important elements. The arbitrary zero point
to which they are referred differs from that adopted here, and com-
parison shows that this may be allowed for by adding 1.9 to Miss
Payne's values of log a_r and 6.3 to those of her later paper. Taking
the mean of her values when she has determined them for two or
more stages of ionization, except that for He^+, which is uncertain,
and comparing with log T from Table XIV, we find the results given
in Table XVI. The value given for H in Table XIV is uncertain,
while Miss Payne's value for K depends on the faint lines λλ 4044,
4047, and is therefore likely to be too low. If these two are rejected,

TABLE XVI

COMPARISON WITH MISS PAYNE'S RESULTS

El.	Miss Payne	Table XIV	Diff.	El.	Miss Payne	Table XIV	Diff.
H........	12.9	[11.5]	(+1.4)	Ca......	6.7	6.7	0.0
He.......	10.2	....	....	Ti......	6.0	5.2	+0.8
Li.......	1.9	2.0	−0.1	V.......	4.9	5.0	−0.1
C........	6.4	7.4:	−1.0	Cr......	5.8	5.7	+0.1
O........	8.0	9.0:	−1.0	Mn.....	6.5	5.9	+0.6
Na.......	7.1	7.2	−0.1	Fe......	6.7	7.2	−0.5
Mg......	7.5	7.8	−0.3	Zn......	6.1	4.9	+1.2
Al.......	6.9	6.4	+0.5	Sr......	3.5	3.3	+0.2
Si.......	7.5	7.3	+0.2	Ba......	3.0	3.3	−0.3
K........	5.3	6.8:	−1.5				

the average difference, regardless of sign, for the other sixteen ele-
ments is ±0.44. This is a very gratifying agreement, especially
when it is considered that Miss Payne's results were determined by
a different theoretical method, with instruments of a quite different
type (Harvard objective prisms), and even on different bodies—a
long list of stars, almost all of which are giants. About the only
common features are the observations of spectral lines and the use
of the ionization theory.

We may next compare the results with the abundance of the
elements in the outer ten miles of the earth's crust,[1] including the
ocean and atmosphere, and in stony meteorites.[2] The results are
exhibited in Table XVII. Here 8.3 has been added to the logarithm

[1] F. W. Clarke and H. S. Washington, *Proceedings of the National Academy of Sciences*, **8**, 114, 1922.

[2] G. P. Merrill, *ibid.*, **1**, 429, 1915.

of the percentage abundance in the earth's crust, and 8.0 to those for the meteorites, to reduce them approximately to the scale of log Q. For the more prominent metallic elements, the relative abundance in the sun resembles that in meteorites more closely than that in the earth's outer layers. The latter show an excess of Al, Si, and Ti, and a deficiency of Mg, which is probably due to the prevalence of granitic rocks. A deeper sample would be composed mainly of the heavy ferromagnesian rocks, and would show proportions more like those in the sun. The deficiency of the alkali metals in the meteorites is conspicuous, but unexplained.

TABLE XVII

ABUNDANCE OF ELEMENTS IN SUN, EARTH, AND METEORITES

El.	Sun	Earth	E−S	Meteorites	M−S	El.	Sun	Earth	E−S	Meteorites	M−S
Na	8.6	8.7	+0.1	7.8	−0.8	Ni	7.8	6.8	−1.0	8.2	+0.4
Mg	9.2	8.6	−0.6	9.1	−0.1	Cu	6.8	6.3	−0.5	6.2	−0.6
Al	7.8	9.2	+1.4	8.2	+0.4	Zn	6.7	5.9	−0.8	....	....
Si	8.8	9.7	+0.9	9.3	+0.5						
K	8.4:	8.7	+0.3	7.2	−1.2	H	11.5:	8.3	−3.2:	6.9	−4.6
Ca	8.3	8.8	+0.5	8.1	−0.2	C	8.5:	7.4	−1.1:	7.2	−1.3
Sc	5.3	3. :	−2. :	....	....	N	8.7?	6.8	−1.9?	....	....
Ti	6.9	8.1	+1.2	7.0	+0.1	O	10.2:	9.7	−0.5:	9.6	−0.6
V	6.7	6.9	+0.2	....	....	F	....	6.8	....	....	....
Cr	7.4	7.1	−0.3	7.5	+0.1	P	....	7.4	....	7.0	....
Mn	7.6	7.3	−0.3	7.3	−0.3	S	7.2:	7.3	+0.1:	8.3	+1.1
Fe	9.0	9.0	0.0	9.4	+0.4	Cl	....	7.7	....	6.9	....
Co	7.4	5.8	−1.6	7.1	−0.3						

Among the non-metals, the figures for N are too uncertain to be of value. Those for C, O, and S indicate a considerable excess in the sun, or deficiency in the earth, while the difference for H is enormous. How much of this is real, and how much due to the uncertainties of the calculation, which are here greater than for any other element, is discussed in §16. It is noteworthy, however, that a discrepancy in this sense, and perhaps a very large one, might be anticipated in just this case. It is probable that the earth and the meteorites were formed by condensation from matter ejected from the sun, as first suggested by Chamberlin and Moulton. The ejected material must have been intensely hot, and would be likely to lose constituents of low atomic weight, hydrogen most of all. Moulton

long ago suggested that the low density of the major planets might be explained by the hypothesis that such losses were less important for the larger bodies. In the outer parts of the sun, on the other hand, there are certain diffusional and electrostatic effects which tend to concentrate the hydrogen at the surface. Thus, for divers reasons, we might expect to find hydrogen much more abundant in the sun's atmosphere than on earth.

Table XVIII gives a comparison of the abundance of the less common elements in the sun and the earth arranged in order of their terrestrial abundance. For those in the first column, Clarke and Washington[1] give specific estimates of percentage. These all appear

TABLE XVIII

ABUNDANCE OF ELEMENTS IN SUN AND EARTH

El.	Sun	Earth	El.	Sun	Earth	El.	Sun	Earth
Ba	5.4	7.2	*Rb*	3.6:	4.5:	*Ag*	3.0	2.5:
Zr	4.5	7.0	*As*	2.5:	4.5:	*Pt*	3.9	1.5:
Sr	5.2	6.8	*Mo*	3.4	4.5:	*Tl*	3.7?	0.5:
Ce, Yt	4.9	6.6	*Sn*	3.3:	4.5:	*In*	2.1:	−0.5:
Li	2.8:	6.0	*Sb*	2.9:	3.5:	*Ga*	3.8:	−0.5:
Pb	3.5	5.6	*Cd*	3.6:	3.5:	*Ge*	4.7	−1.5:
B	5.5?	5.3	*W*	2.5	2.5:			
Be	2.8	5.3	*Cb, Ta*	3.0:	2.5:			

to be much more abundant on the earth than in the sun. It may be that *Ba, Sr*, and some of the others tend to segregate in the granitic surface rocks, as *Ra* is known to do. For the rest, the terrestrial data are rough estimates of the order of magnitude, which agree tolerably with the solar observations, except for the last few elements. It is likely that these, especially *Ga, In*, and *Ge*, are widely disseminated in quantities too minute to be detected by ordinary quantitative analysis, and the same is probably true of *Sc*.

15. *Limits of abundance for elements absent from the solar spectrum.*—We are now in a position to compute superior limits, below which the abundance of the elements not represented in the solar spectrum must lie in order to account for their absence. It appears from Table XII that there are very few instances in which spectral lines are recorded as arising from a term for which the computed

[1] *Loc. cit.*

value of log M is less, algebraically, than -1. Adopting this as the limit of "visibility," we may find by (11) the numbers M_0 and M_1 of neutral and ionized atoms in the normal state (which, in the cases we have here to consider, are usually far greater than any others). If W_0 and W_1 are the weights of the normal states, we have, by (11), setting $M = -1$ for the state which fails to give observable lines:

$$\log M_0 = \log W_0 - \log W + 0.85E - 1 ,$$
$$\log M_1 = \log M_0 - \log W_0 + \log W_1 + I_0 - I . \qquad (12)$$

The limits thus calculated are given in Table XIX. The column headed λ gives the wave-length of the line most likely to appear. When a question mark appears in this column, the most persistent lines from the level under consideration are known to be in the deep red or infra-red, but have either not been analyzed or not observed at all. In these cases, lines in the visible spectrum should also be available, though they are often still unknown. Since these are second members of a series, the tabular values of log Q should be increased for them, probably by about 1. For B, P, and Cs the most promising lines of both the neutral and ionized atoms are included. In calculating log Q, account has been taken, when required, of the relative number of neutral and ionized atoms (log $M_1/M = -1.4$ for B, -2.2 for P, $+4.4$ for Cs, and $+0.5$ for Bi). For Os, which has many low energy-levels, it has been assumed that $S_1 + S_0$ is five times the value of M_0 for the lowest level.

The reason for the absence of most of these elements from the solar spectrum is now perfectly clear. The lowest abundance necessary for the appearance of even their most favorable lines is usually far above the values indicated by their abundance on earth, or by that of elements of similar atomic number in the sun. Only a few cases need special mention.

Boron.—The infra-red lines $3s - 3p$ should appear, but these are so far out as to be accessible only with the bolometer. The pair $3s - 4p$ should be in the yellow and may perhaps be found in the sun, after it has been observed in the arc.

Phosphorus.—The infra-red lines should be near λ 10,000, and the same remark applies to them.

Caesium.—The tabular data refer to the sun's disk. According to our reckoning, the ultimate lines should appear in the spot spectrum, unless $\log Q < 3$. It may be noted, however, that the arc lines of *Ba* do not appear in the spots, although, for its normal state, $\log M = -0.2$. For Cs^+, the excitation potential is so high that there is no possibility of its lines appearing in the sun. The lines at-

TABLE XIX

LIMITS OF ABUNDANCE OF ELEMENTS NOT OBSERVED IN THE SUN

El.	λ	E	log W	log W₀	log M	log Q
He	5875	20.8	0.95	0.30	< 17.1	<17.7
B	?	4.9	0.30	.78	< 3.6	< 4.6
B⁺	3541	9.1	0.48	.30	< 6.6	< 6.2
F	6856	12.6	1.08	.78	< 9.4	<10.7
Ne	6402	16.5	0.95	.30	< 12.3	<13.6
P	?	7.0	1.08	.60	< 4.5	< 6.0
P⁺	5427	10.7	0.95	.95	< 10.0	< 9.3
Cl	8375	8.9	1.08	.78	< 7.2	< 8.8
A	8115	11.6	0.95	.30	< 9.1	<10.7
Se	?	6.0	0.70	.95	< 5.8	< 7.7
Br	?	8.0	1.08	.78	< 6.5	< 8.4
Kr	?	10.0	0.95	.30	< 7.8	< 9.7
Te	?	5.4	0.70	.95	< 4.9	< 7.0
I	?	6.7	1.08	.78	< 5.4	< 7.5
Xe	?	8.4	0.95	.30	< 6.4	< 8.5
Cs	8521	0.0	0.30	.30	< - 1.0	< 5.5
Cs⁺	4603	15.	0.95	.30	< 11.1	<13.2
Os	3058	0.0	....	....	< - 1.0	< 1.7
Au	5837	4.6	0.30	.30	< 2.9	< 5.2
Hg	4046	4.6	0.00	.30	< 3.2	< 5.5
Bi	3067	0.0	0.60	.60	< - 1.0	< 1.9
Ra⁺	3814	0.0	0.30	0.30	< - 1.0	< 1.3

tributed to this element in the *New Rowland* must be accidental coincidences. For *Os* and *Bi* the limit is low, but not so much lower than the observed abundance of the other heavy elements as to cause any serious difficulty. The atomic number of *Os* is even, which makes its rarity somewhat surprising. For *Ra*, in fine, there is ample reason why the actual abundance should be far below the limit here computed.

The result of this survey is, therefore, that the absence of elements from the solar spectrum is completely explicable, quantita-

tively as well as qualitatively, by the structure of their spectra. In a few cases it is probable that the atoms under consideration are less abundant than others of similar atomic weight; but in no case is a great discrepancy necessary to explain the facts. For only two elements—boron and phosphorus—does there appear to be any chance of finding lines in the sun. In both cases, the anticipated lines must first be observed in the laboratory.

There are several additional elements whose presence or absence in the sun cannot at present be definitely determined for lack of laboratory data. These are Ma, Il, Tb, Ho, Tm, Yb, Lu, Ta, Re, Th, and U. All but Yb, Th, and U have odd atomic numbers. Progress for Ta, Th, and U demands the identification of the persistent lines, preferably by the under-water spark; for the rare earths, better wave-lengths are required; while for Ma and Re material for spectroscopic study is not yet available. Some of these metals may yet be found in the sun, but their lines are likely to be very faint.

IV. ASTROPHYSICAL CONSIDERATIONS

16. *The abundance of hydrogen and its consequences.*—The results of the present investigations leave some puzzles to be solved.

a) The calculated abundance of hydrogen in the sun's atmosphere is almost incredibly great.

b) The electron pressures calculated from the degree of ionization and from the numbers of metallic atoms and ions are discordant.

The former method (§11) gave a mean electron pressure P of 3.1 dynes/cm². Milne has shown that the pressure P at the bottom of the effective atmosphere should be twice this, or 6.2 dynes/cm². At the end of §13 we found that the total mass of metallic elements above this level is 42 mg/cm²; that the mean atomic weight is 32; and that 80 per cent of the atoms are ionized. At the sun's surface $g = 2.74 \times 10^4$ cm/sec.², so that the pressure due to the metallic constituents of the atmosphere is 1160 dynes/cm². If no other constituents were present, the electron pressure should be 4/9 of this, or 510 dynes/cm². One of these values is eighty times the other. A similar discrepancy occurs between Unsöld's value determined from the ionization of Ca and that calculated from his figures for its

abundance,[1] and has also been detected in the redder stars by Miss Payne and Mr. Hogg.[2]

The assumption of a higher temperature for the solar atmosphere would diminish this discordance, but by no means remove it. The rather extreme assumption $T = 5740°$ (the effective temperature of the photosphere) gives from ionization $P = 50$ dynes/cm². At the degree of ionization in the atmosphere determined from the arc and spark lines it would be little affected by this change. A discordance by a factor of ten still remains.

c) We may add a difficulty arising from other solar observations. The calculated rate of increase of density with depth in the reversing layer is much more rapid than that indicated by observations of the flash spectrum.

It does not seem to have been noticed that the theoretical difficulties (*b*) and (*c*) can be greatly alleviated, if not removed, by the assumption that the difficulty (*a*) does not exist—in other words, the solar atmosphere really does consist mainly of hydrogen. The solution of (*c*) is obvious. The depth for which the density in an isothermal atmosphere is doubled varies inversely as the mean molecular weight $\bar{m}$. At the sun's surface (with $T = 5000°$) it is $105/\bar{m}$km. A small molecular weight accords much better with the eclipse observations. Menzel, for example, has made a brief report[3] on a determination of the law of decrease of density in the reversing layer by a study of lines in multiplets, which ought to give reliable values.

The writer is greatly indebted to Professor Menzel for permission to state that his unpublished reduction of the Lick Observatory eclipse spectra shows that, in the lower part of the reversing layer, the logarithmic decrement of density, if a temperature of $5000°$ is assumed, corresponds to a mean molecular weight of about 2.

[1] Milne, *Nature*, **121**, 1017, 1928.

[2] *Harvard Circular*, No. 334, 7, 1928. It may be remarked in passing that the criticism which these authors pass (p. 8) on the method of calibration used by Dr. Adams and the writer appears to be needlessly severe, in view of the fact that lines of different elements were used in the two investigations and that there is no theoretical evidence that the effect in question ought to be the same for atoms of different kinds, and good observational evidence that it is not.

[3] *Popular Astronomy*, **36**, 603, 1928.

If only hydrogen and the metals were present, this would determine the abundance of the former. Take the number of metallic atoms per square centimeter as unit, and let H be the number of hydrogen atoms. Since the hydrogen is not appreciably ionized, the whole number of atoms and electrons is then $H+1.8$, and we have $\bar{m}=(H+32)/(H+1.8)$, or for $\bar{m}=2$, $H=28.4$; hydrogen would therefore constitute more than 96 per cent of the atmosphere by volume, and nearly one-half by weight. Now let O and He be the numbers of the corresponding atoms. We have then

$$\bar{m}=(H+4He+16O+32)/(H+He+O+1.8),$$

and if $\bar{m}=2$,

$$H=28.4+2He+14O.$$

According to Table XIV, oxygen is four times as abundant by weight and eight times by volume as all the metals together. Miss Payne (Table XVI) makes it 1.5 times as abundant by volume as all the metals. This determination is probably better than ours, which suffers from difficulties in calibration, and we will assume $O=2$, whence $H=56+2He$. The abundance of helium is very hard to estimate, even in the stars, for its lines appear to be abnormally strong like those of hydrogen, though to a less degree. It is probably conservative to guess that it is at least as abundant as oxygen. Setting $He=2$, we have the results shown in Table XX. Here $\log T$ and $\log Q$ are on the scale of Table XIV. The other non-metals, C, N, S, etc., would probably add but little to the total. These estimates are provisional and will require revision when the density gradient in the flash spectrum is more accurately determined, when the oxygen lines in the deep red are better calibrated, and when—or if—the correction C for departure from thermodynamic equilibrium can be found with less uncertainty.

As they stand, these estimates go a long way toward resolving difficulty (b). The whole pressure due to the solar atmosphere as here contemplated is 4.1 times that due to the metals alone, or 4800 dynes/cm², which is almost 1/200 of an atmosphere, or 3.6 "mm" on the familiar barometric scale; but the electronic pressure is only

0.8/65.8 of this, or 58 dynes/cm². To obtain this value from the
observed ionization we must assume $T = 5800°$, which seems im-
probably high; but none of the factors involved is determined with
any great accuracy, and a tolerable adjustment could be made with
a lower assumed temperature. It appears probable, however, that
the temperature so far assumed for the reversing layer (5040°) is
too low and should be increased to about 5600°. This would raise
the computed level of ionization I_0 to 8.5 volts. The calculated
ratio of the numbers of neutral and ionized atoms would be the same
as before for $I = 6.3$, the average for the elements used in finding I_0.
For larger values of I (*Mg, Fe, Si*), the computed degree of ioniza-

TABLE XX

PROBABLE COMPOSITION OF THE SUN'S ATMOSPHERE

Element	By Volume	By Weight	log T	log Q
Hydrogen............	60 parts	60	9.9	9.9
Helium..............	2 ?	8?	8.4?	9.0?
Oxygen..............	2	32	8.4	9.6
Metals..............	1	32	8.1	9.6
Free electrons........	0.8	0	8.0	....
Total...........	65.8	132	....	....

tion would be slightly increased, but as the changes would affect
log A by 0.2 at most, there is no need to revise Table XIV. With
the higher assumed temperature, the correction C for departure from
thermodynamic equilibrium, determined from the enhanced lines
as before, would be diminished from 1.2 to 0.4 when $E = 8.2$, that is,
from $0.15E$ to $0.05E$, and the computed abundances for the non-
metals would be practically the same as before. With regard to
the intensity of the hydrogen lines, with log $T = 9.9$, and $T = 5600°$,
equation (4) gives, for the two-quantum state, log $M = 1.4$, and
theoretically for Ha, $H\beta$, $H\gamma$, and $H\delta$, log $N = 1.2$, 0.5, 0.0, and
-0.3. The values of log N derived from Unsöld's line contours are
4.1, 3.9, 4.0, and 4.1. To obtain these contours the theoretical num-
ber of atoms must be increased by factors ranging from 800 for Ha
to 25,000 for $H\delta$. Effects peculiar to the hydrogen lines and increas-
ing with the serial number evidently account for a great part of this

discrepancy, but a good deal may remain to be set to the account of some more general departure from thermodynamic equilibrium.

17. *Note on the departure from thermodynamic equilibrium.*—Professor Eddington, in a letter which he has generously given permission to quote, makes a very important suggestion regarding the excess of intensity of lines of high excitation potential. This phenomenon, which is especially conspicuous when the redder giant stars are compared with the sun, was attributed by the writer[1] to a progressive increase in the number of excited atoms, compared with the number for thermodynamic equilibrium. Eddington writes:

I am convinced that the right interpretation is exactly the opposite—that there are too few highly excited atoms. The argument is very simple, and the reason you differ is that you considered the formation of the line as a matter of absorption only without considering the emission. Suppose e.g. that the number of atoms in states

$$1, \ 2, \ 3, \ 4 \ . \ . \ . \ .$$

were　　　　　　　　　　　　$1, \ 2, \ 4, \ 8 \ . \ . \ . \ .$ times the proper equilibrium numbers. Then considering the absorption line $3 \rightarrow 4$ you evidently have 4 times the equilibrium amount of absorption but 8 times the equilibrium amount of emission in this line. Naturally the excessive emission will tend to wash out the line and perhaps even make it a bright line. On the other hand if the numbers were

$$1, \ \tfrac{1}{2}, \ \tfrac{1}{4}, \ \tfrac{1}{8} \text{ of the equilibrium numbers there}$$

is an actual loss of the $4 \rightarrow 3$ radiation (absorbed and not re-emitted in the same wave-length). This is much more effective in producing dark lines than the ordinary process of turning radiation backwards, which produces the line as a sort of second order effect.

Modifying the investigation in §§ 234–235 of *The Internal Constitution of the Stars*, he writes:

Omitting ϵ for simplicity, but inserting a factor $\gamma (< 1)$ representing reduced emission due to defect of atoms in the upper of the two states, I find instead of (235.4)

$$H' = aH \left(\frac{k}{k'} + \frac{p \left(1 - \frac{k}{k'} \right)}{p + \tfrac{3}{2}} \ e^{-pr'} \right)$$

where　　　　　　$a = \dfrac{k}{k'(1-\gamma) + \gamma k} \qquad p^2 = \dfrac{3(k'(1-\gamma) + \gamma k)}{k'} \ .$

[1] Adams and Russell, *Mt. Wilson Contr.*, No. 359; *Astrophysical Journal*, **68**, 20, 1928.

Retaining only the largest terms this gives at the boundary

$$H'/H = \tfrac{2}{3}ap \qquad (\text{cf. [238.1]})$$

$$= \frac{2}{\sqrt{3}} \frac{k}{\sqrt{k'(k'(1-\gamma)+\gamma k)}} \,.$$

Thus for $\gamma = 1$

$$H'/H = \frac{2}{\sqrt{3}} \sqrt{\frac{k}{k'}}$$

for $\gamma = \tfrac{1}{2}$

$$H'/H = \frac{2}{\sqrt{3}} \sqrt{2}\, \frac{k}{\sqrt{k'(k'+k)}} = \frac{2}{\sqrt{3}} \sqrt{2}\, \frac{k}{k'} \quad \text{approximately.}$$

Since $k':k$ is large (ratio of absorption coefficients inside and outside the line) the latter gives much deeper blackening than the former.

I do not think you will need large deviations from the equilibrium proportions to account for your results, remembering that the introduction of differential emission and absorption is much more potent than a mere increase of both.

It seems much more easy to account for a defect of highly excited atoms than an excess—perhaps due to removal of the extreme ultra-violet radiation by continuous absorption which I expected would be shown in the sun's spectral energy curve though apparently the later determinations do not seem to bear it out. Again a spectrum of the principal lines of the element is being formed in the ordinary way and this, of course, means there is less radiation available to bring the atoms to the highly excited states. (It is, however, not obvious that this would give a *progressively decreasing* number in the higher states.) However, whether easily explicable or not, I think this is the immediate deduction from the results you have reached.

The importance of distortion of the sun's energy-curve has recently been pointed out by Gerasimovič,[1] who has shown that local weakening of the spectrum in the near ultra-violet, leaving the remoter part little affected, would lead to an excess of atoms in the highly excited states.

Such a distortion of the energy-curve seems improbable; but a progressive weakening in the remoter ultra-violet, beyond the region accessible to our observation, is more likely. The lines of the principal series beyond which general absorption might be expected to set in are at λ 2850 for K, λ 2420 for Na, and λ 2030 for Ca, and so on, and beyond these one would expect depression in the energy-

[1] *Monthly Notices, R.A.S.*, **89**, 272, 1929.

curve similar to that which exists beyond the Balmer limit in A stars.

Another possibility deserves discussion. Compare a solar atmosphere composed solely of metallic atoms (neutral and ionized) and electrons with another which contains the same numbers of each of these constituents in each unit of volume diluted with an excess of hydrogen. The hydrogen atoms will be practically all neutral and almost inert, except that collisions between them and the excited metallic atoms will tend to bring the latter back to states of lower energy. In thermodynamic equilibrium, the effect would be balanced by excitation by collisions with fast-moving hydrogen atoms. In the reversing layer, however, the number of excitations by photospheric radiation exceeds that in an atmosphere in thermodynamic equilibrium, and it would appear that the intensity of a dark spectral line should be greater when most of these additional excited atoms are discharged by collisions of the second kind, than when they unload their energy by radiation. It is well known that the effective collision radii of excited atoms are large, and, if they increase, as is probable, for the more highly excited states, the differential effect which is observed might be accounted for.

This qualitative argument is not presented as conclusive, but in the hope that the problem will be attacked in detail by some competent investigator.

18. *A new case in Milne's ionization equations.*—Milne, in a very important paper,[1] has proved that under very varied conditions the ratio of the total numbers of neutral and ionized atoms of a given element above any specified level in a stellar atmosphere will be very nearly equal to that computed from a simple Saha formula, on the assumption of a mean pressure one-half of that at the base-level. The principal simplifications are that the atmosphere is treated as isothermal and radiation pressure is neglected. His Problem IV, in which the atoms considered are in presence of an excess of atoms of a different ionization potential, is similar to our present case, but in his solution, he assumes that practically all the electrons come from the ionization of the abundant element, which is not the case in a solar atmosphere rich in hydrogen. The general formulae

[1] *Ibid.*, p. 17, 1928.

are simple and may be given here. If N_0, N_1 are the numbers of neutral and singly ionized atoms of the first element per square centimeter above the given level, and $N = N_0 + N_1$, $x = N_1/N$, we have

$$\frac{N_1}{N_0} = \frac{x}{1-x} = \frac{K}{P}, \qquad x = \frac{K}{P+K}, \tag{13}$$

where K is the ionization factor, which is given in our notation by

$$\log_{10} K = -\frac{5040 I}{T} + \tfrac{5}{2} \log T - 6.5, \tag{14}$$

and is constant, since the atmosphere is isothermal. Now let N', X', K', etc., refer to the atoms of the second element and let ϵ and $\epsilon' = 1 - \epsilon$ be the relative *numbers* of atoms of the two kinds and m the mean atomic weight. We have, then, for the total pressure, $p = (N + N')mg$, whence

$$N = \frac{\epsilon}{mg} p. \tag{15}$$

Milne has shown that

$$N_1 = \frac{\epsilon}{mg} \int_0^p x \, dp. \tag{16}$$

Now

$$\frac{p}{P} = 1 + \frac{1}{\epsilon x + \epsilon' x'} = 1 + \frac{(P+K)(P+K')}{P(\epsilon K + \epsilon' K') + KK'} = 1 + \frac{(P+K)(P+K')}{Q(P+R)}$$

where

$$Q = \epsilon K + \epsilon' K', \qquad R = KK'/Q.$$

Hence

$$dp = dP + (P+K)d \frac{P(P+K')}{Q(P+R)} + \frac{P(P+K')}{Q(P+R)} \, dP.$$

Introducing this into (16), we find

$$N_1 = \frac{K\epsilon}{mg} \left\{ \log\left(1 + \frac{P}{K}\right) + \frac{P(P+K')}{Q(P+R)} + \frac{P}{Q} + \frac{1}{Q} \int_0^p \frac{P(K'-K-R) - KR}{(P+K)(P+R)} \, dP \right\} \tag{17}$$

$$= \frac{K\epsilon}{mg} \left\{ \frac{P(2P+K'+R)}{Q(P+R)} + \frac{K(Q-K)}{Q(K-R)} \log\left(1 + \frac{P}{K}\right) - \frac{R(K'-R)}{Q(K-R)} \log\left(1 + \frac{P}{R}\right) \right\},$$

$$N_1 = \frac{K\epsilon}{mg} \left\{ \frac{P(2P+K'+R)}{Q(P+R)} + \frac{\epsilon'}{\epsilon} \left[\log\left(1 + \frac{P}{K}\right) - \frac{R^2}{K^2} \log\left(1 + \frac{P}{R}\right) \right] \right\}. \tag{18}$$

With this and

$$N = \frac{\epsilon}{mg} P \left\{ 1 + \frac{(P+K)(P+K')}{Q(P+R)} \right\} , \tag{19}$$

the general problem is solved.

We are concerned at present, however, with the case in which K' is negligibly small. Setting $K' = 0$, we have $Q = \epsilon K$, $R = 0$. Equation (17) still holds good, but the integral takes a different and much simpler form, giving

$$\left. \begin{aligned} N_1 &= \frac{1}{mg} \left\{ 2P - (1-\epsilon)K \log \left(1 + \frac{P}{K} \right) \right\} , \\ N &= \frac{1}{mgK} \left\{ \frac{P^2}{K} + (1+\epsilon)P \right\} , \\ N_0 &= \frac{1}{mg} \left\{ \frac{P^2}{K} - (1-\epsilon)P + (1-\epsilon)K \log \left(1 + \frac{P}{K} \right) \right\} . \end{aligned} \right\} \tag{20}$$

If we write $P/K = z$, the effective electronic pressure is given by

$$\bar{P} = \frac{KN_0}{N_1} = P \frac{z^2 - (1-\epsilon)\{z - \log (1+z)\}}{2z^2 - (1-\epsilon)z \log (1+z)} . \tag{21}$$

Whenever $\epsilon = 1$, $\bar{P}/P = \frac{1}{2}$. The greatest deviation from this ratio occurs when $\epsilon = 0$ and z is about 3, when $\bar{P} = 0.535P$. The approximation $\bar{P} = P/2$ is remarkably good under all circumstances.

19. *Applications to the stars.*—The assumption of an atmosphere composed mainly of hydrogen serves also to resolve some difficulties which appeared in the study of stellar spectra made last year by Adams and the writer.[1] The electronic pressures, computed from the relative strength of the arc and enhanced lines, came out about 10 times greater in Procyon and 60 times greater in Sirius than in the sun, while the amounts of metallic vapor above equal areas of surface were 0.6 and 0.05 times as great. Allowance for double ionization in Sirius would increase the last figure, but could hardly double it. It was then suggested that a great abundance of hydrogen in Sirius might explain these facts, but the full effect was not realized. At the temperature of an A star, hydrogen must be heavily ionized. If the hydrogen atoms are as abundant as has been sug-

[1] *Mt. Wilson Contr.*, No. 359; *Astrophysical Journal*, **68**, 9, 1928.

gested for the sun, there are dozens of them for every metallic atom, and, when a considerable fraction of these are ionized, the electronic pressure may be many times that which would arise from the ionization of the metallic atoms alone. At the same time, these electrons and the hydrogen ions contribute to the general opacity, so that the photosphere is raised and the total quantity of gas above it is much diminished, and the metallic lines are thus weakened.

Hydrogen must be extremely abundant in the atmosphere of the red giants, for its lines are stronger in their spectra than in that of the sun. With any reasonable allowance for the effect of the lower temperature in diminishing the proportion of excited atoms, the relative abundance of hydrogen, compared with the metals, comes out hundreds of times greater than in the sun. If this is true, the outer portions of these stars must be almost pure hydrogen, with hardly more than a smell of metallic vapors in it.

The theory of such an atmosphere presents an interesting problem, for quantities which are ordinarily neglected may have to be considered—for example, scattering by the unexcited neutral atoms. The effect of hydrogen in reducing the electronic pressure in the sun appears to be already near its limiting value, and it cannot be invoked further to account for the extraordinary discrepancy in these stars between the degree of ionization indicated by the enhanced lines and the pressure calculated from the extent of the atmospheres and the surface gravity. Discussion of these matters, however, cannot be undertaken in the present paper.

In conclusion, it should be emphasized that the present work, like that of Dr. Adams and the writer last year, is of the nature of a reconnaissance of new territory. It is to be hoped that the determinations made here by approximate methods will be replaced within in a few years by others of much greater precision, based on accurate measures of the contours and intensities of as many lines as possible. An extensive field of work is open, and it is hoped that much more may be done at this Observatory.

It is a pleasure to express the writer's indebtedness for the use of the great mass of manuscript dealing with solar lines, multiplets, and the like, which has been collected by Dr. St. John and Miss

Moore; to Messrs. E. F. Adams and Theodore Dunham, Jr., for friendly aid in the tabulation of some of the material; and especially to Professor Eddington for the suggestion quoted in §17, and to Professor D. H. Menzel for the unpublished data mentioned in §16.

TABLE XXI

REFERENCES FOR SPECTROSCOPIC DATA

Element	I	II	Element	I	II	Element	I	II
H......	1	....	Fe.....	4, 65, 95	4, 69	Te.....	55	....
He.....	1	1	Co.....	4, 21	4, 63	I......	93	....
Li.....	1	80, 96	Ni.....	4, 7, 75	4, 50, 83	Xe.....	6, 41	....
Be.....	10, 68	10	Cu.....	1, 81	4, 50, 82	Cs.....	1	....
B......	11, 78	9, 17	Zn.....	1	4, 94	Ba.....	1	1
C......	31	27, 32	Ga.....	1	49	La.....	5, 60	61
N......	23, 46	28, 30	Ge.....	34	51	Ce.....	5	....
O	1, 43	73	As.....	56	....	Pr.....	5	....
F......	26	12	Se.....	1, 55	....	Nd....	5	....
Ne.....	3	74	Br.....	93	....	Sa.....	5	....
Na.....	1	16	Kr.....	6	....	Gd.....	5	....
Mg....	1	1	Rb.....	1	....	Tb.....	5	....
Al.....	1	66, 79	Sr.....	1	1	Dy....	5	....
Si....	29, 33	29	Yt.....	62	62	Yb....	5	....
P.....	56	13	Zr.....	2, 48	2, 48	W.....	52, 53	....
S......	1, 18, 42	44	Cb.....	2	2	Os.....	59	....
Cl.....	24	14, 67	Mo....	45	2	Ir.....	59	....
A......	64, 77	22, 25	Ru....	88	....	Pt.....	40, 59	....
K......	1	15	Rh....	89	....	Au....	91	....
Ca.....	1	4, 76	Pd....	8, 84	86	Hg....	1	19
Sc.....	4, 70	4, 70	Ag.....	1	85	Tl.....	1	87
Ti.....	4, 72	4, 71	Cd.....	1	94	Pb.....	35	36
V.....	4, 57, 63	4, 58	In.....	1	....	Bi.....	92	....
Cr.....	4, 48	4, 47, 48	Sn.....	37, 90	38	Ra.....	....	1
Mn....	4, 20	4	Sb.....	39, 54	....			

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REVIEWS

A Short History of Physics. By H. BUCKLEY. London: American Agents, D. Van Nostrand, Inc., Methuen & Co. 1927. Pp. xi + 263. $3.00.

The avowed object of the author has been to "present the theories of modern physics as illustrative of scientific thought and as essentially developments from the successes and failures of earlier investigators"; and apparently to provide at the same time an exposition of physical science for the general reader. As a consequence, the book is not addressed primarily to the professional physicist and only a general acquaintance with scientific terminology is presupposed, while in the main the treatment is descriptive rather than critical.

Whether the author's contention that the historical method offers advantages over the more usual logical presentation must remain a matter of opinion. To the reviewer it appears that the first two-thirds of the book, devoted to the concepts of classical physics, might well serve as an interesting and attractive first introduction to physics for a mature reader. The chapters on modern atomistics, relativity, and radiation theory, however, appear too condensed to be very easily intelligible to one not previously acquainted with the subject matter. The book will probably find its greatest usefulness as supplementary reading to a college course in physics, where a text of this sort is almost essential.

Though concise, the treatment is in general very clear. An interestting feature is the insertion of many citations from original papers and treatises, although as a rule these are quite brief. The inclusion of more biographical material and the addition to the text of a few figures and portraits would have served to enliven the book and quicken the interest of the student. The last chapters contain an account of the main features of the Bohr theory, but there is no mention of the new quantum dynamics.

F. C. HOYT

Three Lectures on Atomic Physics. By ARNOLD SOMMERFELD. Translated by HENRY L. BROSE. New York: E. P. Dutton & Co., 1926. Pp. 70. 8 diagrams. $3.00.

These lectures, entitled "General Remarks on Atomic Physics, and in Particular on the Spectra of Hydrogen and Helium," "The General Spectrum of the Complex Terms," and "Chemical Bonds and Crystal Struc-

ture," were delivered at the University of London in 1926. This, it will be recalled, was the year of the publication of Schrödinger's first papers on the wave mechanics. They contain, however, only brief mention of the new quantum mechanics and the importance of Schrödinger's contributions, after which the first two lectures are devoted to a discussion of the formal interpretation of the structure of line spectra on the basis of the older form of the quantum theory. In spite of the limitations of space we have here a surprising amount of information, presented in Professor Sommerfeld's usual lucid style. Fortunately, this will prove as valuable now as at the time it was written, for although there have been rapid advances in atomic physics in the interim, the schematic classification of line spectra has remained almost unaltered. Considerable attention is given to the question of nomenclature, and that recommended coincides with what is now most generally used.

The first two lectures provide an excellent introduction to a more detailed study of complex line spectra. The last lecture is somewhat more special, treating of some aspects of the completion of subgroups of electronic orbits as reflected in spectra and the formation of compounds and crystals.

F. C. HOYT